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CHARACTERIZATION OF THE UPTAKE OF NITROGEN OXIDES ON ALUMINA ADSORBENTS

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ENVIRONMENTAL ENGINEERING SCIENCE
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MAY 1999

MASTER OF SCIENCE THESIS
MARCH 1998 TO JANUARY 1999

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13. ABSTRACT *(Maximum 200 words)*

The objective of this research was to develop a method that employed ion-specific electrodes (ISEs) to quantify nitrate and nitrite (NOx) in aqueous solutions that contained NOx exposed alumina and to correlate the quantities of these surface NOx species with the quantity of gaseous NOx sorbed. The final objective was to obtain material balances of NOx sorbed to nitrate and nitrite formed and to observe indicative relationships between the surface and gaseous species which may lead to the establishment of possible adorrption mechanisms.

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ABSTRACT

Previous research has shown that adsorption of NO_x on alumina sorbents is enhanced when these sorbents are treated (coated) with compounds consisting of group-I carbonates and hydroxides. NO_x sorption on alumina sorbents has been suggested to form nitrate and nitrite species on the sorbent surface. Studies were undertaken to quantify the nitrate and nitrite that is formed on alumina sorbent surfaces. This study focused on three alumina sorbents: untreated alumina, and alumina treated with either potassium carbonate (K_2CO_3) or potassium hydroxide (KOH). A method that employed ion-specific electrodes (ISEs) was developed for the quantification of nitrate and nitrite species formed on the sorbents.

Through the coordination of gaseous NO_x uptake data and corresponding quantities of nitrate and nitrite (NO_x^-) formed on the sorbent surface, general mechanisms of NO_x sorption have been developed for untreated, K_2CO_3-treated and KOH-treated γ-alumina.

Based on the data, two initial sorption processes occur in which either NO_2 sorption alone occurs or simultaneous NO and NO_2 sorption occurs. NO_2 sorption results in nitrate and nitrite formation. Simultaneous NO and NO_2 sorption results in nitrite formation. Subsequent NO_2 exposure converts the initially formed nitrite to nitrate and gaseous NO. Nitrite-to-nitrate conversion is dependent on the stability of surface nitrite. Significant NO sorption occurs on treated aluminas. For treated aluminas, increased NO sorption occurs at higher temperatures (up to 250 °C) and results in greater nitrite formation. Untreated alumina does not sorb NO and treated aluminas do not sorb NO in the absence of NO_2.

EXECUTIVE SUMMARY

A. OBJECTIVE

The objective of this research effort was to develop a method that employed ion-specific electrodes (ISEs) to quantify nitrate and nitrite (NO_x^-) in aqueous solutions that contained NO_x-exposed alumina and to correlate the quantities of these surface NO_x^- species with the quantity of gaseous NO_x sorbed. The final objective was to obtain material balances of NO_x sorbed to nitrate and nitrite formed and to observe indicative relationships between the surface and gaseous species which may lead to the establishment of possible adsorption mechanisms.

B. BACKGROUND

The USAF has sponsored studies at the University of Florida which have investigated novel forms of NO_x control using sorptive materials. A solid sorbent, magnesia-coated vermiculite (MgO/v), has been applied to control NO_x from USAF combustion sources and performed marginally due to its low sorption capacity. Kimm (1995) proposed that MgO actively sorbed NO_2 forming NO in a 3:1 ratio and nitrate based on studies of heterogeneous NO_x chemistry. Given the results of these studies, additional work was recommended to further develop this applicable and simple method of NO_x control. Studies by Lee et al (1998a and 1998b) have shown that γ-alumina is a much better sorbent for NO_x than MgO/v, particularly when the alumina is treated with carbonates or hydroxides of the group-I elements. As Kimm (1995), Lee et al. (1998a and 1998b), and other researchers have observed the formation of nitrate and nitrite during NO_x sorption, studies were initiated to quantify these two species from NO_x-exposed alumina sorbents on the premise that this knowledge would help to determine the mechanisms of sorption.

C. SCOPE

This report is a thesis presented to the University of Florida in partial fulfillment of the requirements for the master of science degree in environmental engineering science. The report describes the details, results, and conclusions of laboratory tests regarding the ISE measurements of nitrate and nitrite and the correlation of these to gaseous NO_x sorbed. Important gas-phase relationships determined by Lee (1999) are also related, as they are essential to this investigation. This investigation was focused on three alumina-based sorbents: untreated alumina, K_2CO_3-treated alumina, and KOH-treated alumina.

D. METHODOLOGY

NO_x-exposed alumina samples were obtained from Maxwell Lee (University of Florida) who directed the gaseous exposures of NO_x to the sorbents in a fixed-bed dynamic reactor

system with data collection by a chemiluminescent NO_x analyzer. Separate ISE methods were developed for quantifying nitrate and nitrite formed on the alumina sorbents upon exposure to NO_x. The gaseous uptake data was obtained from Lee and correlated to the nitrate and nitrite data obtained from the ISE measurements and general sorption mechanisms were proposed for the three sorbents.

E.   TEST DESCRIPTION

Alumina samples (dry pellets) were obtained from Maxwell Lee who directed the gaseous exposures to NO_x under different temperatures from (25 to 250 °C) and gas stream compositions (varying NO and NO_2 concentrations). The exposed alumina samples were placed in aqueous solutions to allow for measurement of electrochemical potential due to the quantities of nitrate and nitrite present. Nitrate and nitrite ISEs were used to measure the electrochemical potential of the alumina solutions in a half-cell with a reference electrode supplying a baseline potential. Standard solutions simulated the compositions of the actual sample solutions. Measurements of pH were also performed on the alumina solutions.

F.   RESULTS

The ISE methods for nitrate and nitrite quantification tended to overestimate surface NO_x^- present on the treated sorbents and tended to underestimate surface NO_x^- present on the untreated sorbents, sometimes by as much as 20%. The best percent recoveries (100%) from NO_x sorbed to NO_x^- formed were obtained when the alumina samples were tested immediately after exposure in the reactor bed. The pH of the alumina solutions was primarily dependent on the treatment compound and was slightly dependent on the nitrate concentration of the solution. The pH ranges were 4-6, 10-11, and 11-12 for untreated, K_2CO_3-treated, and KOH-treated aluminas, respectively, with solutions having greater nitrate concentrations displaying a pH in the lower end of these ranges. Typically, there was at least twice as much NO_x^- present on the treated aluminas than on untreated alumina for similar exposures which corresponds to the enhanced NO_x sorption capabilities of the treated aluminas. For untreated alumina, nitrite was present in small quantities and did not increase with exposure whereas much more nitrate was present, and nitrate quantities increased with exposure. For the treated aluminas, both nitrite and nitrate were present in greater quantities and nitrite formation was favored initially. As exposure to NO_2 increased, nitrate formation was favored on the treated aluminas and the characteristic NO production was observed. These observations suggest that the nitrite that was formed initially is later converted to nitrate and NO is produced in this conversion. The characteristic production of NO was noted almost immediately upon NO_x exposure to untreated alumina and was effectively delayed when the treated aluminas were used.

G.   CONCLUSIONS

The proposed mechanisms of NO_x sorption by the three materials were supported though the correlation of gaseous uptakes and the corresponding surface NO_x^- formed on the sorbent surfaces. For the treated aluminas, sorption of NO was significant and was favored at higher temperatures and/or increased NO concentrations in the gas stream. NO sorption by untreated alumina was minimal. As exposure time increased, the characteristic NO production was observed for all three alumina-based sorbents although this action was effectively delayed when the treated alumina sorbents were used. This delay in NO production for the treated aluminas is likely due to the greater thermal and chemical stabilities of the potassium nitrite which is formed on the treated aluminas compared to the relative instability of aluminum nitrite which is formed on untreated alumina.

H.   RECOMMENDATIONS

It is imperative that the alumina samples be tested immediately after they are exposed in the reactor bed. As time in storage increases, degradation of the NO_x^- species and variation in test results also increase. Degradation in NO_x^- species was found to be significant after a storage time of one day. Attempts at improving the overall accuracy of the ISE methods through the use of ionic strength adjusters and/or buffer solutions may be worthwhile. Though the ISE methods are advantageous in regards to prompt instrumental response and system simplicity, the preparation of standards and samples to ensure reliable results (through pH balancing) is time consuming. Also, no reliable method was found to preserve the standard solutions without interfering with the ionic strength of the solutions and so fresh standards had to be made daily. Automated methods such as ion chromatography (IC) would be more efficient for long-term, large volume projects, though a reliable filtration system would be needed to prevent fine alumina particles in the sample solutions from fouling the IC system.

CHARACTERIZATION OF
THE UPTAKE OF NITROGEN OXIDES
ON ALUMINA ADSORBENTS

By

DAVID A. POCENGAL

A THESIS PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

UNIVERSITY OF FLORIDA

1999

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of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Master of Science

CHARACTERIZATION OF
THE UPTAKE OF NITROGEN OXIDES
ON ALUMINA ADSORBENTS

By

David A. Pocengal

May, 1999

Chairman: Dr. Eric R. Allen
Major Department: Environmental Engineering Sciences

Quantification of nitrate and nitrite species on NO_x-exposed alumina is essential to

understanding the mechanism of NO_x sorption on this material. Studies were undertaken

to determine the role of nitrate and nitrite species in the mechanisms of NO_x adsorption on

three types of alumina adsorbent materials. By relating surface nitrate and nitrite

concentrations to sorption of gaseous NO_x, relationships can be observed between the

gaseous and surface species which can lead to the establishment of adsorption

mechanisms.

A method using ion-specific electrodes (ISEs) was developed for quantifying

nitrate and nitrite concentrations on alumina exposed to NO and NO_2 (NO_x) gas. Nitrate

and nitrite ISEs were used. Three alumina sorbent types were tested: untreated, K_2CO_3-

treated, and KOH-treated alumina.

Through the coordination of gaseous NO_x and surface NO_x^- data, sorption mechanisms were proposed for each of the three materials. A ratio of 3 moles of NO_2 sorbed to 1 mole of NO produced was evident for the materials tested. NO is not significantly sorbed by untreated alumina. NO is sorbed initially by the treated materials when NO_2 is also present in the airstream. Sorption of NO does not occur on the treated materials if NO_2 gas is not present. A simultaneous reaction involving NO, NO_2, and the treatment compound is indicated by this observation. Conversely, sorption of NO_2 on any of the materials tested does not require that NO be present, which suggests an additional reaction between NO_2 and the sorbent.

The enhanced sorption of NO_x by the alkaline sorbents suggests that alumina is better suited in the role of a support material for sorptive compounds rather than as an active adsorbent . Potassium carbonate was more efficient than potassium hydroxide in sorbing NO_x. The characteristic production of NO, observed in the sorption of NO_x by the three materials tested, was delayed the longest for K_2CO_3-treated alumina and was also delayed, though to a lesser extent, for KOH-treated alumina. NO production was observed almost immediately for untreated alumina upon initial exposure to NO_x.

The proposed mechanisms are supported by observations of gaseous NO_x uptakes and the associated formation of nitrate and nitrite on the sorbent surfaces. Significant sorption of both NO_2 and NO by the alkaline-treated sorbents was observed in these investigations. Sorption of NO is favored at higher temperatures and/or with airstreams consisting of increased amounts of NO relative to NO_2. This increased sorption of NO is associated with an increase in the formation of nitrite on the treated sorbent surfaces.

CHAPTER 1
INTRODUCTION

The emission of nitrogen oxides, particularly NO and NO_2, which are referred to as NO_x, from both stationary and mobile sources is an important issue in air quality concerns. High levels of NO_x emissions are associated with increased ambient NO_x concentrations which can cause detrimental effects to the human respiratory system as well as to vegetation. NO_2 reacts with water vapor in the atmosphere to form nitric acid and, hence, contributes to acid rain. Also, NO_x is a major precursor in photochemical processes which lead to the formation of ozone in the troposphere. Additionally, high NO_2 concentrations in air form a brownish haze which diminishes visibility while being aesthetically displeasing. Most anthropogenic NO_x emissions result from the burning of fossil fuels, particularly from electric power plants, motor vehicles, and industrial sources.

NO_x Formation

To develop a means of controlling NO_x emissions, it is necessary to understand how these nitrogen oxides are formed in combustion processes. NO_x is formed by two general pathways: (1) the conversion of chemically-bound nitrogen in the combusted fuel ('fuel' NO_x) or by (2) thermal fixation of atmospheric nitrogen in the combustion air ('thermal' NO_x).

When a fuel containing organically-bound nitrogen is burned, such as coal or oil, the contribution of the fuel-bound nitrogen to the total NO_x production is significant. The N-C bond in the fuel is considerably weaker than the N-N bond in molecular nitrogen, which allows for the oxidation of the 'fuel' nitrogen to NO by oxygen in the combustion gas. Though the kinetics and mechanisms of this process are not completely understood, it has been established that the air/fuel ratio plays a major role in 'fuel' NO production. As the air/fuel ratio increases, the percent conversion of fuel nitrogen to NO also increases. The degree of fuel-air mixing also strongly affects the percent conversion of fuel nitrogen to NO, with greater mixing resulting in greater percent conversion. Small variations in temperature do not readily affect NO_x production from fuel nitrogen (Cooper and Alley, 1994).

Thermal NO_x is produced when hot gas in the combustion zone mixes with ambient air. The hot gas supplies energy to break the O-O bond in molecular oxygen, allowing for the consequent oxidation of a nitrogen molecule by atomic oxygen. The basic steps in this reaction were first established by Zeldovich in 1946:

$$N_2 + O^- \leftrightarrow NO + N \qquad\qquad (1\text{-}1)$$

$$N + O_2 \leftrightarrow NO + O \qquad\qquad (1\text{-}2)$$

$$N + OH \leftrightarrow NO + H \qquad\qquad (1\text{-}3)$$

$$CH + N_2 \leftrightarrow CHN + N \qquad\qquad (1\text{-}4)$$

It is assumed in the above reactions that the fuel combustion reactions between C_xH_y and O have reached equilibrium and that the concentrations of O, H, and OH can be described by equilibrium equations. If only thermodynamic considerations of NO_x formation are taken into account, stoichiometric relationships can be outlined:

$$N_2 + O_2 \leftrightarrow 2NO \qquad\qquad (1\text{-}5)$$

$$NO + \tfrac{1}{2}\,O_2 \leftrightarrow NO_2 \qquad\qquad (1\text{-}6)$$
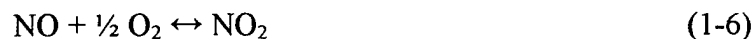
The equilibrium constants for reaction (1-4) and (1-5), K_{p1} and K_{p2}, respectively, are:

$$K_{p1} = (P_{NO})^2 / (P_{N2})\,(P_{O2}) = (Y_{NO})^2 / (Y_{N2})\,(Y_{O2}) \qquad (1\text{-}7)$$

$$K_{p2} = (P_{NO2}) / (P_{NO})\,(P_{O2})^{1/2} = (P_T)^{-1/2}\,(Y_{NO2}) / (Y_{NO})\,(Y_{O2})^{1/2} \quad (1\text{-}8)$$

where

K_p = equilibrium constant
P_i = partial pressure of component i (atm)
Y_i = mole fraction of component i
and P_T = total pressure (atm)

Values for the equilibrium constants represented in equations (1-7) and (1-8) at various temperatures are presented in Table 1-1. From Table 1-1 it can be seen that in general, the formation of NO is favored at higher temperatures and the formation of NO_2 is favored at lower temperatures. However, the differences in equilibrium constants at the various temperatures warrant closer inspection in terms of what is actually occurring for the two reactions in question. It can be seen that at temperatures lower than 1000°K, very little NO is produced. However, the rate of equilibrium NO formation increases rapidly with increasing temperature, particularly when operating below 1000°K. The formation of NO_2 is heavily favored at temperatures below 1000°K. At temperatures above 1000°K, the rate of NO formation still increases with increasing temperature, though at a lower rate compared to increasing temperatures below 1000°K. NO production is still favored over that of NO_2 at temperatures above 1000°K. Also, at these higher temperatures, NO_2 dissociates to NO, further adding to the total NO produced in combustion. NO formed by

reaction (1-1) has a very high activation energy (317 kJ/mole) when compared to the other reactions and is most likely the rate-controlling reaction (Ismagilov et al., 1990).

Table 1-1. Equilibrium Constants for the Formation of NO and NO_2 (Source: Cooper and Alley, 1994).

Temperature		$\underline{K_p}$	
$\underline{°K}$ $\quad$ $\underline{°F}$		$\underline{N_2 + O_2 \leftrightarrow 2\ NO}$	$\underline{NO + \tfrac{1}{2}\ O_2 \leftrightarrow\ NO_2}$
300	80	10^{-30}	$1.4(10)^6$
500	440	$2.7(10)^{-18}$	$1.3(10)^2$
1000	1340	$7.5(10)^{-9}$	$1.2(10)^{-1}$
1500	2240	$1.1(10)^{-5}$	$1.1(10)^{-2}$
2000	3140	$4.0(10)^{-4}$	$3.5(10)^{-3}$
2200	3500	$3.5(10)^{-3}$	$2.6(10)^{-3}$

Calculated equilibrium concentrations of NO and NO_2 from reactions (1-5) and (1-6) are presented in Figure 1-1. In actual furnace emissions, concentrations of NO_x proposed in Table 1-1 and Figure 1-1 are not observed. NO_x concentrations measured in exhaust gas at large coal-fired power plants are typically 300-1200 ppm and NO/ NO_2 ratios vary from 10:1 to 20:1 (Cooper and Alley, 1994). This 'prompt' NO formation may be due to super-equilibrium radical concentrations which likely exist in hydrocarbon flames (Bowman, 1975; Fenimore, 1971). Prompt NO is more important in fuel-rich combustion zones (Cooper and Alley, 1994). It is likely that the intermediate, hydrogen cyanide (HCN), is formed when N_2 is attacked by hydrocarbon radicals that are formed during flame combustion. HCN combines with OH to form CN, then CN is oxidized to NO. Also, N atoms and NH radicals are formed and can be oxidized to NO in the flame (Flagan
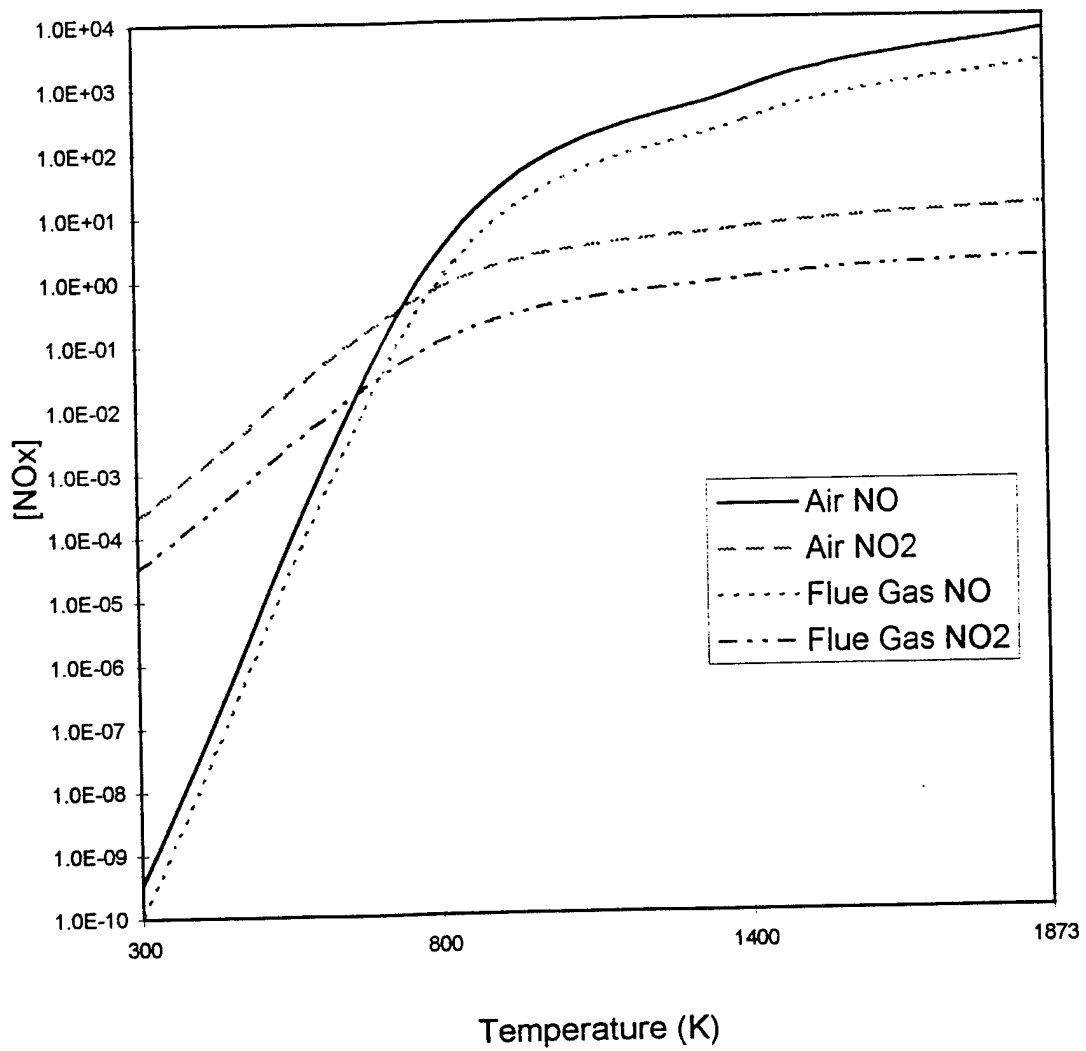
Figure 1-1. Calculated Equilibrium Concentrations (ppm) of NO and NO2 in Air and Flue Gas (Source: Cooper and Alley, 1994)

and Seinfeld, 1988). MacKinnon (1974) developed a model which predicts the concentration of NO formed during combustion as a function of temperature, time, and concentrations of N_2 and O_2. At a pressure of 1 atm, the model equation is

$$C_{NO} = 5.2(10)^{17} [\exp - 72{,}300/T] \, Y_{N2} \, Y_{O2}^{1/2} \, t \qquad (1\text{-}9)$$

where

C_{NO} = NO concentration, ppm
Y_i = mole fraction of component i
T = absolute temperature, °K
and t = time, s

While equation (1-8) does not consider the presence of other atoms and radicals, which can significantly affect the NO formation rate, it is sufficient to explain the differences between observed and expected NO_x concentrations. Equation (1-8) allows insight into how NO formation is affected by the flame-zone temperature. As exhaust gases move away from the flame zone they cool rapidly, reducing the reaction rates by orders of magnitude, particularly for the conversion of NO to NO_2, which is kinetically limited. This has the effect of essentially 'freezing' the concentrations of NO and NO_2 at the levels which were formed initially (Cooper and Alley, 1994). Thus, as high concentrations of NO are formed in the high temperature flame zone, about 90-95% of NO_x emitted in the exhaust gas appears as NO (Cooper and Alley, 1994; Wark and Warner, 1994).

Equation (1-8) provides some insight into strategies for the control of thermal NO_x. The peak temperature should be reduced, the gas residence time at the peak temperature should be reduced, and the oxygen concentration in the zone of highest temperature should be reduced (Cooper and Alley, 1994).

Approaches for NO_x Control

Historically NO_x control has been both a difficult and expensive process. Most control methods include the modification of the combustion process and/or post-combustion removal. Presently there exist several combustion modifications which are in use for NO_x control at stationary sources. These include low-excess air (LEA) firing, which limits the amount of O_2 available to oxidize N_2 to NO; off-stoichiometric combustion (OSC), which combusts fuel in two steps—an initial fuel-rich flame zone and a secondary fuel-lean zone; flue gas recirculation (FGR) where the flue gas is reburned in the furnace; gas reburning where natural gas or other fuel is injected above the furnace to form a 'reburn' zone—here hydrocarbon radicals react with NO_x formed below to reduce the NO_x to molecular nitrogen; also water injection can be effective in reducing flame temperatures and thus, formation of thermal NO_x. Note that these techniques are only useful for furnaces and other stationary sources which burn large amounts of coal or oil.

Post-combustion control techniques, or flue gas treatment (FGT) methods, often have higher NO_x removal efficiencies than combustion controls and are most often used where combustion controls are not applicable, such as in chemical processing. FGT methods are broadly classified as dry and wet methods. Dry methods include catalytic and non-catalytic reduction and adsorption. Wet methods include wet scrubbing (absorption) processes.

Wet scrubbing processes can be used to remove both NO_x and SO_x. These methods involve the oxidation of NO to NO_2 (as NO has low solubility in water) and/or the use of a chemical-enhanced (caustic) scrubbing liquid. These systems have been shown to be somewhat useful, though they suffer from pH sensitivity. Also, these systems

have a high capital cost and the handling/disposal of the spent scrubbing liquid is also a major environmental concern.

Selective catalytic reduction (SCR) is the most advanced dry FGT method and is more popular in Japan than in the U.S. In SCR, a reducing gas such as NH_3 is vaporized and injected into the flue gas in the presence of a catalyst to reduce NO_x to N_2. Titanium and vanadium oxide pellets are often used as the catalyst. Typical reduction efficiencies are about 80%. SCR suffers from temperature sensitivity, which can lead to increased NO_x emissions or emission of the reducing gas, if operating outside of the optimal temperature range. Catalyst fouling is another concern at coal-fired power plants (Cooper and Alley, 1994).

Selective non-catalytic reduction (SNCR) uses higher temperatures ($900-1000\,^\circ C$) to reduce NO_x to N_2 without a catalyst. Again, NH_3 is most often used as the reducing gas. Reduction efficiencies range from 40-60%. SNCR is more susceptible to temperature variations than SCR. If the temperature is too low the ammonia will not completely react and will be emitted. If the temperature is too high ammonia will be oxidized to NO (Cooper and Alley, 1994).

Adsorption, particularly dry sorption, has been proposed and demonstrated for control of both NO_x and SO_x. Several materials have been tested including activated carbon and copper oxide. Some of these systems have used NH_3 as a reducing gas, often in the presence of a catalyst. Recently a few organizations have tried to develop an adsorbent material which will effectively remove NO_x from flue gas without the use of a catalyst or injection of a reducing gas. This method of NO_x control is attractive as it is relatively inexpensive compared to other post-combustion methods outlined previously in

this thesis. Also, incorporation of an adsorption system does not involve major system modifications as with other control techniques. A reusable sorbent material, if effective, would offer a relatively cheap and simple alternative for NO_x control when other options are considered, particularly for sources in which combustion processes are not easily or practically controlled. Dry sorption methods have several advantages including ease of material handling and low maintenance requirements. Several dry sorbent materials have been found to effectively remove NO_x over a greater range of operating conditions than catalytic reduction methods without the occurrence of adverse emissions or requirement for necessary monitoring controls (Nelson et al., 1992). An inexpensive, widely available sorbent with known sorptive characteristics could find application to numerous small NO_x emission sources as a low capital cost control method (Lee et al., 1998a).

Jet Engine Test Cells

Federal and state emission limits for NO_x have been established and are continually being lowered for various stationary and mobile sources. One type of source which is not currently regulated but which may be in the near future are jet-engine test cells (JETCs) which emit high levels of NO_x under certain operating conditions. Evolving regulations, particularly the 1990 Clean Air Act Amendments (CAAA), along with the failures of existing NO_x control measures and the correlation between elevated ozone levels and NO_x concentrations point toward increased regulatory pressure to reduce NO_x emissions from JETCs in the near future (Kimm, 1995). In fact, the U.S. EPA organized a committee under Title IV of the CAAA, which produced recommendations regarding the regulation of JETCs as stationary sources (Kimm, 1995).

Conventional methods of NO_x control through combustion modifications were not applicable to JETCs due to the large range of operating conditions and strict performance standards required during testing (US EPA, 1994). Therefore, post-combustion exhaust gas treatment (FGT) was determined to be the most applicable method of controlling NO_x emissions from these sources (Kimm et al., 1995). Hence, the USAF has provided funding for studies concerning novel forms of NO_x control, which may be applicable to JETCs. Since 1990 the United States Air Force (USAF) has supported research at the University of Florida into the use of adsorbent materials in JETCs for NO_x control.

Previous Research

Since JETCs are operated by the USAF, this agency has been primarily responsible for the funding and development of efforts for controlling NOx emissions from these sources. In the latter half of the 1980's the USAF began funding projects to explore novel NO_x control processes which could be applicable to JETCs. The method proposed as the best available control technology (BACT) at that time was SCR. The drawbacks of SCR in application to JETCs were documented by early investigators (Nelson et al. 1989, 1992). The large temperature range under which JETCs are operated requires elaborate process controls to minimize ammonia slip. Back pressure created by placement of control mechanisms in the exhaust train affected the jet engine performance. The price of consuming the precious metal catalyst (platinum, rhodium, palladium, etc.) was equally discouraging (Nelson et al. 1989, 1992).

Of seven developmental projects funded by the USAF, only one showed promising results (Kimm, 1995; Kimm et al., 1995). This particular study was conducted

by Sanitech (Twinsburg, OH) and considered a relatively inexpensive and readily available material. vermiculite, as a replacement catalyst in the SCR system. Vermiculite was found to effectively reduce NO_2 (to N_2 and O_2) without the addition of ammonia gas. With only the vermiculite catalyst, NO_2 reduction of 50-73% was noted over a temperature range from 250 to 850F. Vermiculite coated with MgO and $MgSO_3$ (without added ammonia gas) improved NO_2 reduction to 70-88% (Nelson et al., 1989). This action was initially considered to be catalytic (Nelson et al., 1989) but was later classified as adsorptive (Nelson et al., 1993; Kimm, 1995). Sorption of NO was minimal for all vermiculite sorbents (Kimm, 1995)

Although vermiculite coated with MgO (MgO/v) showed some promising results, its applicability to JETCs was hindered by the build up of back pressure in the test cell. When the MgO/v filter was placed in the cell perpendicular to the exhaust gas flow NO_x was effectively removed. However, the pressure drop created by the filter was too high and caused the temperature in the cell (and engine) to rise, which affected the engine's performance. When different baffle designs were devised to decrease the filter pressure drop the removal of NO_x was minimal (Nelson et al. 1992, 1993). A large filter system was eventually designed by Sorbent Technologies Corp. (Twinsburg, OH) to fit on the end of the test cell exhaust which was deemed both feasible and practical for use in such an application.

Studies by Lee et al. (1998a and 1998b) at the University of Florida showed that gamma (γ) alumina was a better sorbent of NO_x (both NO and NO_2) than MgO/v. Gamma-alumina is a high-surface-area sorbent, is inexpensive and readily available, and has been shown to have effective adsorptive properties as well as being a durable catalytic

support (Kirk-Othman, 1992; Lee et al., 1998a and 1998b). Laboratory-scale testing showed that γ-alumina was a better sorbent for NO_x than MgO/v and that when the alumina was coated (treated) with either potassium carbonate or potassium hydroxide, its adsorptive properties for NO_x control were significantly enhanced (Lee et al., 1998a and 1998b). Lee et al. (1998a) also noted that when compared to a similar filter bed of MgO/v, the alumina bed had a 20% lower pressure drop. The system and conditions used by Lee are described in detail elsewhere (Lee, 1998; Lee et al., 1998a, 1998b).

During Lee's studies (Lee, 1998; Lee et al., 1998a) it was noted that in some test runs NO was taken up (sorbed) but that after a certain time, NO was observed to be produced. It was determined that after substantial NO_x sorption, for every three NO_2 species taken up, one NO was produced. This was also reported by Kimm (1995) and Kimm et al. (1995) in his work with MgO/v. Nelli and Rochelle (1996) reported similar findings and ascribed them to reactions of sorbed water and NO_2 on the surface of alumina and proposed the following mechanism:

$$3NO_{2(g)} + H_2O_{(l)} = 2HNO_{3(l)} + NO_{(g)} \tag{1-10}$$
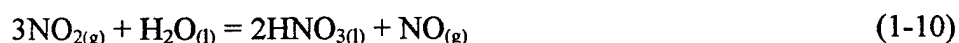
According to Nelli and Rochelle (1996) the production of NO is based on the vapor-liquid equilibrium values of nitric acid. Alkaline solids, such as $Ca(OH)_2$, buffer the pH of the sorbent and alter the formation of NO. Such a sorbent would prevent both HNO_2 and HNO_3 from dissociating and consequently reduce NO production. Similarly, reduced NO production from alkaline-treated alumina (compared to untreated alumina) was observed by Lee (1998) and Lee et al. (1998a and 1998b).

A 3-step mechanism for the adsorption of NO_2 on MgO/v and the consequent production of NO was proposed by Kimm (1995):

$$NO_{2(g)} + MgO_{(s)} \rightarrow MgNO_{3(s)} \qquad (1\text{-}11)$$

$$NO_{2(g)} + MgNO_{3(s)} \rightarrow Mg(NO_2)NO_{3(s)} \qquad (1\text{-}12)$$

$$NO_{2(g)} + Mg(NO_2)NO_{3(s)} \rightarrow Mg(NO_3)_{2(s)} + NO_{(g)} \qquad (1\text{-}13)$$
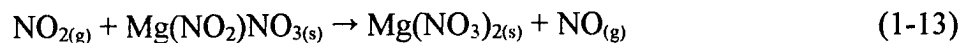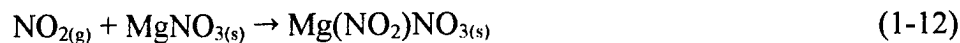
The overall reaction can be written:

$$3NO_{2(g)} + MgO_{(s)} \rightarrow Mg(NO_3)_{2(s)} + NO_{(g)} \qquad (1\text{-}14)$$
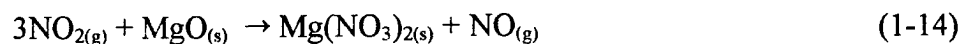
Both mechanisms given by equations (1-10) and (1-14) state that 3 moles of NO_2 are

sorbed to form 2 moles of nitrate or nitric acid species (depending on pH) and 1 mole of

NO. Boehm (1972) has explained the formation of nitrate ions resulting from NO_2

sorption on alumina as a result of disproportionation of surface OH⁻ ions with NO_2:

$$[OH^-]_{surf} + 3NO_2 = [NO_3^-]_{surf} + HNO_3 + NO \qquad (1\text{-}15)$$
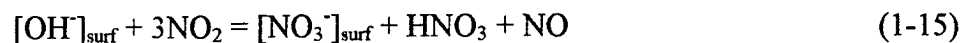
The formation of NO via this mechanism again agrees with observations of NO_2 sorption

on other oxides and with the reported molar ratios of NO_2 removal to NO formation as

3:1 (Lee et al., 1998a).

During Lee's (1998b) study, when samples of KOH-treated alumina were exposed

to NOx and underwent XPS (X-ray Photoelectron Spectroscopy) analyses to determine

the nature of the species present on the surface, both nitrate and nitrite species were

observed. This reaffirms suggestions by Knozinger (1976) that NO_2 adsorbs to γ-alumina

as nitrate and/or nitrite species. Krizek (1966) determined that the absorption of NO_2 by

aqueous KOH produced potassium nitrite. He also found that aqueous KOH was more

effective in absorbing NO_2 than aqueous NaOH. Similarly, studies by Lee et al. (1998b)

determined that potassium compounds were more effective than sodium compounds in

sorbing NOx.

Current Research Justification

Though γ-alumina has been shown to be an effective sorbent for NO_x, little is known about the nature of the adsorption process and the associated chemical reactions which occur at the alumina- NO_x interface. Nitrate and nitrite species are undoubtedly present but in what capacity they serve is less certain. These species may have a role, either active or passive, in the adsorption of NO_x on treated and untreated γ-alumina. Quantitative, temporal, and other analyses of nitrate and nitrite species present on exposed alumina samples may provide information involving the effectiveness and/or mechanisms of the NO_x adsorption process. Considering that NO_x is sorbed on the alumina sorbent surface(s) as either nitrate or nitrite species, it may be possible to observe the nature of the interactions which exist between gaseous NO_x and the solid alumina surface (treated and untreated) by coordinating gaseous NO_x uptake data with information regarding the quantities of nitrate and nitrite species present on exposed samples. Analyses of nitrate and nitrite on the exposed alumina surface should be helpful in this respect. Also, the determination of hydrogen ion activity at the alumina surface through the measurement of pH may be informative in regards to the nature of species present during NOx adsorption, as exemplified in equations (1-10) and (1-14).

Research Objectives

Based upon the justification for research, the objectives of this study are to

1. Develop a reliable method for the measurement of nitrate and nitrite species in aqueous extracts of NO_x -exposed untreated and treated alumina samples..

2. Measure hydrogen ion activity on the surface of exposed alumina through pH measurement in aqueous solutions.

3. Obtain material balances for gaseous NO_x species entering and leaving the reactor system used to expose alumina to NO_x and correlate with species present on the alumina surface.

4. Observe important interactions and/or propose mechanisms based on results for the adsorption of NO_x by untreated and treated aluminas in objectives 1.-3.

CHAPTER 2
EXPERIMENTAL METHODS AND MATERIALS

Preliminary investigations into the development of methods to measure nitrate, nitrite, and hydrogen ion species present on exposed alumina began early in 1998. Max Lee, who ran the reactor studies as part of his Ph.D. research program, provided exposed (to NO_X) samples of alumina, in the form of pellets to be analyzed. To enable measurement of the species under investigation, specific portions of the alumina sample were put into solution with a known quantity of de-ionized water. After sonication, the solutions were prepared for analysis. Standard operating procedures (SOPs) were developed using synthetic samples in order to generate reliable and reproducible results. These SOP's are included in Appendix A.

The pH of the solution was measured directly with a pH combination-electrode. Measurements of nitrate and nitrite concentrations posed more of a challenge. Few reliable and simple methods for nitrate and nitrite assays exist. While Ion Chromatography (IC) is often used for this application this option was ruled out. The major concern with this method was with the alumina samples being particularly turbid which could lead to problems of column and system fouling if adequate filtering was not achieved. EPA method 353.2 for nitrogen as nitrate/nitrite is often used in water sampling. Though this is the generally accepted method for aqueous nitrate/nitrite, it is a fairly complex process involving several chemical derivitizations and complexing agents.

This method quantifies NO_x^- species through spectrophotometric measurement of a colored nitrite complex. Nitrate is reduced to nitrite in a reduction column containing granulated copper and cadmium. The nitrite is diazotized with sulfanilamide and complexed with N-(1-naphtyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured spectrophotometrically. The turbidity of the exposed alumina samples would cause an interference with this measurement technique.

Ion-Specific Electrodes (ISEs) are often used in the quantification of common anions present in various solution matrices. ISEs have several advantages over other instruments used for analyses of industrial samples. They have a fast response and are precise. Also, they are not susceptible to interferences due to sample color, viscosity, or suspended solids (Thomas, 1980). As sonication of the exposed alumina sample solutions turned the solutions an opaque gray color, and with obvious suspended solids also present, ISEs were favored as the analytic tool of choice.

ISE Background

ISEs are used as a relatively simple and reliable instrument for the quantification of many different ions. They are especially useful where sample solutions often contain suspended solids and colored components. Since its inception into regular use in the 1970's, the nitrate ISE has been used for nitrate quantification in various sample matrices which include vegetable and meat products, sugar, soil, water, and other plant materials (Milham et al., 1970; Sweetsur et al., 1975; Choi et al., 1980; Karim et al,. 1986; Bednar et al., 1991; and others). Morie et al., 1972 quantified nitrate and nitrite from cigarette

smoke dissolved in NaOH solution with the Orion Nitrate ISE. The nitrite ISE is a relative newcomer, being first commercially produced in the 1990s.

The use of ISEs is noted more in Europe and Asia than in the United States. This may have to do with the fact that ISEs are popular to smaller markets as they represent a small fraction of the capital investment required for more complex systems used in trace analyses. For this same reason. ISEs are attractive for short-term projects and where prompt results are desired. An ISE measuring system, which consists of the required electrodes and an appropriate display meter, is readily portable. With proper care an ISE system may return reliable results for several years (Orion Research, 1996).

ISEs are used to measure the electrochemical potential of aqueous solutions. A typical ISE consists of an electrode body and a replaceable sensing module. The sensing module contains a liquid internal filling solution in contact with a gelled, organophillic membrane containing an ion exchanger specific to a particular ion. A typical ISE and pH/mV meter are shown in Figure 2-1. When the membrane of the module is in contact with a solution containing ions which can pass through the ion exchanger, an electrode potential develops across the membrane. This potential, which depends on the level of the free ion (activity) in solution, is measured against a constant reference potential (supplied by a reference electrode) with a digital pH/mV meter. The measured potential corresponding to the level of the ion in solution is described by the Nernst equation:

$$E = E_0 - S \log(A) \tag{2-1}$$

where

E = measured electrode potential, mV
E_0 = reference potential (constant), mV
A = ion level in solution (activity)

and   S = electrode slope (about -53 to -60 mV per decade increase)

The level of specific ion, A, is the activity or 'effective concentration' of that particular ion

in solution. The total concentration of the specific ion in solution includes both bound or

complexed ions as well as free (unattached) ions:

$$C_F = C_T - C_B \qquad\qquad (2\text{-}2)$$

where

C_F = concentration of free ions
C_T = total ion concentration
and C_B = concentration of ions in bound or complexed forms
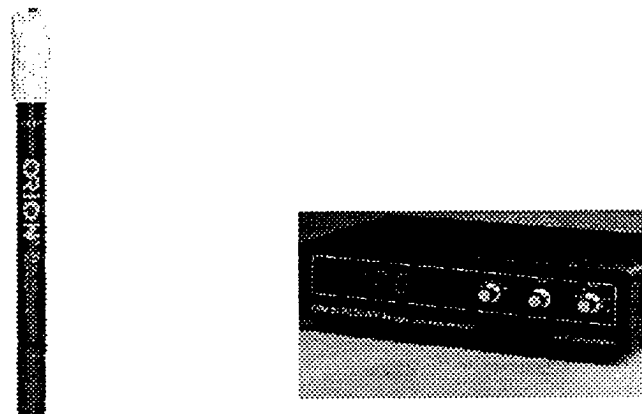
Figure 2-1. Typical Ion-Specific Electrode and pH/mV meter

The ion activity is related to the free ion concentration by the activity coefficient (γ):

$$A = \gamma \, C_F \qquad\qquad (2\text{-}3)$$

Ionic activity coefficients are variable and largely depend on total ionic strength. Ionic

strength is defined as

$$IS = \frac{1}{2} \sum C_1 Z_1^2 + C_2 Z_2^2 ... C_i Z_i^2 \qquad (2\text{-}4)$$

where

IS = ionic strength
C_i = concentration of ion i
and Z_i = charge of ion i

If the background ionic strength is high and constant relative to the sensed ion concentration, the activity coefficient is constant and the activity is directly proportional to concentration. In order to equalize the ionic strength between the sample and the standard solutions, the latter were designed to simulate the composition of the sample solution. This will be discussed in greater detail in the following sections describing the methods for nitrate and nitrite analysis. ISE's for both nitrate and nitrite are currently available and were used in this investigation.

Background and Measurement of pH

The degree of acidity in a sample is most typically quantified through pH measurement. The definition of pH is

$$pH = -\log [H_3O^+] \qquad (2\text{-}5)$$

where the concentration is in moles per liter. The lower the pH of a sample, the greater the acidity of that sample.

The system used for pH measurement was a combination pH electrode (Accumet model 13-620-AP50, Pittsburgh, PA) and portable pH meter (Fisher Scientific model AP-61, Pittsburgh, PA). The system was calibrated by using standard pH buffer solutions of pH 4, 7, and 10 (Fisher Scientific, Pittsburgh, PA). After sonication of a sample, pH was measured directly with the pH electrode. Experimental data for pH, nitrate, and nitrite

determinations were recorded in pre-made tables labeled as 'TEST SHEET', see
Appendix B.

Measurement of Nitrate

Nitrate was measured with a nitrate ISE (Orion model 93-07, Beverly, MA) in a
half-cell with a double-junction reference electrode (Orion model 90-02). The inner
solution of the reference electrode consisted of Ag/AgCl solution (Orion 900002) while
the outer solution was a dilute solution of nitrate Ionic Strength Adjustor (Orion 930711).
The two electrodes were connected to a pH/mV meter Corning (model 245, Corning, NY)
set to measure mV. Nitrate measurements always preceded those for nitrite (see the
'Nitrite Measurement' section).

Measurement of nitrate with the Orion nitrate ISE is impeded by pH limitations
and by interferences with nitrite (and other anions which were not present in quantities
sufficient to cause interferences). In order for accurate measurements to be obtained and
to keep the ISE module membrane from breaking down, the pH of measured solutions
should be between 2.5 and 11 (Orion Research, 1991). Also, since nitrite was present in
samples, it was necessary to remove this interference. This was done through the addition
of sulfamic acid (HSO_3NH_2) to the sample solution. Sulfamic acid reacts with nitrite by
the following reaction:

$$HSO_3NH_{2(aq)} + NO_2^-{}_{(aq)} \rightarrow N_{2(g)} + SO_4^-{}_{(aq)} + H_3O^+{}_{(aq)} \qquad (2\text{-}6)$$
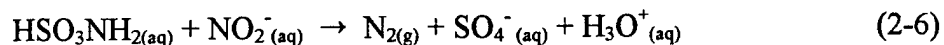
A strong sulfamic acid solution (about 1M) was added to standards and samples and the
pH monitored with the pH electrode. The pH of the standards and samples was set at 2.5.
Volume changes were recorded. Calibration and direct measurement of the sample then
proceeded.

22

In order to simulate the composition of the sample alumina solutions, different standards (and methods) were used for each sample-type. The sample types are defined by the type of treatment of the alumina. Standard solutions were made by dissolving a known amount of magnesium nitrate in a known volume of DI water to obtain a solution of .1M nitrate and performing serial dilutions of this solution to concentrations of .05M, .01M, .005M, .001M, and .0001M. There was no difference in the measured cell potentials of nitrate solutions with equal concentrations which were made using different nitrate compounds ($Mg(NO_3)_2$, $NaNO_3$, KNO_3).

Untreated Alumina

Preliminary testing demonstrated that in order to obtain adequate recovery of NO_x^- species (with comparison to gaseous NO_x uptake data) from the surface of untreated alumina, it was necessary to crush the pellets into powder. The pellets were powderized using a small mortar and pestle. The mortar and pestle used were composed of inert volcanic glass and were washed with DI water and dried with forced air between sample measurements. The powder was weighed and then put into aqueous solutions of 50 or 100 mL. The solution was sonicated for 10 minutes. After sonication, a portion of the sample was poured into a 50 mL beaker. The pH was measured and then the volume recorded. The pH of the standards and samples were adjusted to 2.5 and calibration and direct measurement proceeded as outlined above.

K₂CO₃-treated Alumina

The pH of these particular alumina solutions were generally in the range from 10 to 11. In order to approximate the ionic strength of the sample, K_2CO_3 solution was added to pure nitrate standards until the pH was equal to the pH of the sample. Sulfamic acid was then added in excess until either any reaction observed (the sulfamic acid reacting with nitrite to form nitrogen gas which bubbles out of solution) was complete or until the pH of the sample was below 2. In a sample of low nitrite concentration (roughly < .001M) no reaction will be observed, whereas the converse is true for samples of higher nitrite concentration (roughly > .001M). K_2CO_3 solution is added to the sample after the addition of the sulfamic acid to bring the pH to 2.5. Calibration and measurement then proceeded and volume changes were noted.

KOH-treated Alumina

The pH of these particular alumina solutions were generally in the range from 11 to 12. The procedure was the same as that for K_2CO_3-treated alumina, except that KOH was substituted for K_2CO_3.

Measurement of Nitrite

Nitrite was measured with a nitrite ISE (Orion model 93-46) in a half-cell with a single-junction reference electrode (Orion model 90-01). The fill solution of the reference electrode consisted of Orion Optimum Results F Filling Solution (900046) consisting of a proprietary ingredient. The two electrodes were connected to a pH/mV meter (Corning

model 245) set to measure mV. A portion of the sample (unadulterated) was used in the testing. Standard solutions were obtained in the same manner as outlined in the above 'Measurement of Nitrate' section, using nitrite compounds in place of nitrate compounds. Cell potentials in solutions of equal nitrite concentrations were the same for solutions made with either $NaNO_2$ or KNO_2.

Measurement of nitrite is also limited by pH restrictions and anion interferences. The working pH range of the Orion Nitrite ISE is 4 to 8. Optimum results are obtained at pH 4-4.5 (Orion Research, 1996). The presence of nitrate in a sample interferes with nitrite measurement. Since no reliable method was found (or was available) to remove the nitrate, the nitrite standards used in the calibration were contaminated with nitrate to the same level as determined in the sample by the nitrate analysis. This is the reason why nitrate concentration is measured before that of nitrite. pH adjustments, calibration of standards, and sample measurement then proceeded in this order.

Untreated Alumina

The pH of these samples were generally in the range from 4 to 6. After contamination of the nitrite standards with nitrate to the level of nitrate determined in the sample, the pH of the standards were set according to the pH of the sample. If the pH of the sample was greater than 4.5, sulfuric acid was added to both the sample and the standards to an equal pH between 4 and 4.5. If the pH of the sample was between 4 and 4.5, sulfuric acid was added to the standards corresponding to the pH of the sample. Calibration and direct measurement proceeded.

K$_2$CO$_3$-treated Alumina

After the nitrite standards were contaminated with nitrate to the level of nitrate determined in the sample, the pH of the contaminated nitrite standards were adjusted with K$_2$CO$_3$ solution to the pH of the sample. Sulfuric acid was then added to each standard until the pH was at a corresponding value between 4 and 4.5 for all standards. The sample pH was then adjusted to the pH of the standards with sulfuric acid, and, if needed, K$_2$CO$_3$ solution. Volume changes in the standards and the sample were recorded. Calibration and direct measurement then proceeded.

KOH-treated Alumina

The procedure for these samples was the same as that for K$_2$CO$_3$-treated alumina except KOH is substituted for K$_2$CO$_3$.

Other Materials

Alumina (type T-3438, Engelhard, Elyira, OH) was in pellet form (1/8 in. diameter and 1/8 in. length). An analytical balance (Ohaus model CT10, Florham Park, NJ) was used for obtaining weights of the chemical compounds and alumina samples. De-ionized water was obtained through a Barnstead (Boston, MA) Nanopure II system set at 17 MΩ-cm. All chemicals used were Fisher Scientific reagent grade. A Fisher Scientific Stirring Hot Plate was used to stir solutions. Specific volume pipettes and beakers as well as graduated cylinders were used for volumetric determinations.

Quality Control

Testing of samples were done according to sample type (treatment type) and nitrate/nitrite (NO_x^-)concentrations. In order to facilitate the testing process and save time, samples which were of the same type and which were thought to be similar in total NOx^- species concentration, upon consultation with Max Lee, were tested on the same day so that one set of standards could be used for the samples to be tested. In this way sample testing was done in 'batches' of similar samples which were examined on one specific day using the same standard solutions.

In order to ascertain the degree of accuracy of a testing day (or batch of samples) an independent sample of known nitrate and nitrite concentrations was made up, which had the same characteristics as the actual samples that were tested on that day. This independent sample was analyzed by the same procedure as that for the actual samples. For example. suppose that KOH-treated alumina samples are being tested which have nitrate and nitrite concentrations of around .001M and .01M, respectively. After all the samples have been analyzed, an independent sample is made which may have nitrate and nitrite concentrations of .002M and .01M, respectively. KOH-treated alumina (unexposed) is added into the independent sample solution to adjust its pH to be close to that of the actual samples tested. After sonication, the independent sample is tested in the same way as for the actual samples. Data are recorded for the independent samples on sheets labeled 'QC TEST SHEET', see Appendix B. Percent recovery is calculated from the known and determined nitrate and nitrite concentrations of the independent sample. These percent errors are presented in a control chart for the dates of testing, see Appendix C.

CHAPTER 3
RESULTS AND DISCUSSION

The analyses considered three alumina-types: untreated, potassium carbonate-treated, and potassium hydroxide-treated. Each of these types of samples showed differing proportions of nitrate/nitrite which, with the inclusion of the NO_x uptake data supplied by Max Lee, led to the proposal of mechanisms for the reactions of NO_x at the alumina surface. However, before results from the actual testing are discussed, it is necessary to outline findings of preliminary investigations into the characteristics of the ISE testing method. The first section of this chapter will pertain to the components and methods used in the actual testing method. These findings provided important observations and practical considerations with regard to the testing components and their effect on obtaining accurate results using the aforementioned procedures. The rest of the chapter is dedicated to a discussion of the test results from exposed alumina samples.

Background Investigations: Method Parameters

It was necessary to determine if the components of the sample solutions had any effect on the cell potential measurements. In order to address these questions, simple tests were designed which focused on individual solution components and any related measurement anomalies.

Water Studies

De-ionized (DI) water was used exclusively for all standards and samples. Testing for NO_x^- species in the DI water yielded no measurable amounts present. Consideration was also given to the presence of dissolved oxygen which may oxidize NO_2^- to NO_3^-. Equivalent low-level NO_2^- samples were made in both unaltered DI water and DI water which was deoxygenated. The deoxygenated water was made by bubbling nitrogen gas through a flask of DI water while boiling. The results showed no difference in measured NO_2^- concentrations.

Alumina Studies

Two important qualities regarding the alumina pellets required investigation. The first involved the degradation of NO_x^- species present on the surface of the alumina pellets over time. The second considered if the presence of alumina in the sample solutions had any effect on the measured cell potential.

Alumina 'shelf life'

It was important to determine whether or not the NO_x^- species present on the alumina surface, particularly NO_3^-, would degrade over time. After exposure in the reactor bed, the alumina pellets (dry) were placed in polystyrene vials for storage. In order to determine if degradation was occurring while in storage, alumina samples were tested once and then reanalyzed one month later, that is, a portion of the alumina pellets from a particular exposure to NO_x were tested and the rest of the pellets from the sample were stored (dry) for one month. After one month the remaining pellets were tested. Five

samples each of differing exposures (with varied quantities NO_3^- and NO_2^- present) were tested in this way for untreated, K_2CO_3-treated, and KOH-treated alumina samples. The results of these tests are shown in Table 3-1. The measured nitrate and nitrite concentrations have been converted to moles per gram alumina, since concentration is subject to the relative amounts of solute and solvent in solution. (Note: 'moles' refers to gram-moles throughout this thesis). These samples are from a fixed reactor bed which consisted of fifteen grams of sorbent. The bed was divided into five 3-gram layers which were analyzed separately for nitrate and nitrite species. This particular bed arrangement, referred as the 'longbed', was used for many of the analyses outlined in this thesis and will be discussed more in the following sections. In Table 3-1 it can be seen that a significant decrease in nitrate and nitrite (NO_x^-) surface quantities occurred over a period of one month for untreated and potassium carbonate-treated alumina. The results for KOH-treated alumina in Table 3-1 show a slight monthly increase in nitrate and nitrite on the surface of KOH-treated alumina. This is likely due to random error inherent in the test method. It is possible that KOH, being a stronger base than K_2CO_3, may prevent nitrate and nitrite degradation by effectively shielding these compounds from microbial activity. Note that there was considerable variation in the changes in NO_x^- quantities over the one month period. More about this is described in following sections.

Effect of alumina on NO_x^- measurement

When actual samples are tested, sonication leaves the sample solution very turbid due to the physical breakdown of the alumina pellets. Though this turbidity factor was not

Table 3-1. Degradation of Nitrate and Nitrite on Dry Alumina Pellets: Nitrate and Nitrite Moles per Gram Alumina Measured at a 1-Month Interval

UNTREATED	Initially		After 1 Month		% Change	
Sample	NO3-	NO2-	NO3-	NO2-	NO3-	NO2-
1	0.000033	8.4E-06	0.00002	8.2E-06	-39.4	-2.4
2	0.000044	8.3E-06	0.000031	8.4E-06	-29.5	1.2
3	0.00013	0.000014	0.0001	8.6E-06	-23.1	-38.6
4	0.00024	0.00001	0.0002	8.4E-06	-16.7	-16.0
5	0.00032	7.9E-06	0.00028	4.8E-06	-12.5	-39.2
				Ave =	-24.2	-19.0
				SD =	10.7	19.3

K₂CO₃	Initially		After 1 Month		% Change	
Sample	NO3-	NO2-	NO3-	NO2-	NO3-	NO2-
1	0.000031	0.00015	0.000018	0.00011	-41.9	-26.7
2	0.000065	0.00022	0.000035	0.00014	-46.2	-36.4
3	0.00017	0.00024	0.00018	0.0002	5.9	-16.7
4	0.00031	0.00021	0.00031	0.00022	0.0	4.8
5	0.00066	0.00024	0.00051	0.00019	-22.7	-20.8
				Ave =	-21.0	-19.2
				SD =	23.7	15.3

KOH	Initially		After 1 Month		% Change	
Sample	NO3-	NO2-	NO3-	NO2-	NO3-	NO2-
1	0.000024	0.00014	0.00002	0.00011	-16.7	-21.4
2	0.000047	0.00016	0.00005	0.00017	6.4	6.3
3	0.00011	0.00019	0.00013	0.00022	18.2	15.8
4	0.00037	0.00019	0.00036	0.00021	-2.7	10.5
5	0.00044	0.00017	0.00047	0.00018	6.8	5.9
				Ave =	2.4	3.4
				SD =	13.0	14.4

suspected of being an interference with aqueous NO_x^- measurements, tests were designed

to determine if the presence of alumina had any effect on the cell potential readings. To

accomplish this, samples of known concentrations of NO_3^- and NO_2^- were tested

repeatedly with and without alumina present in the solution. Figures 3-1, 3-2, and 3-3

show the percent error associated with measurements for three different sample mixes for

the three sample types (treatments). The concentrations of the samples were: (1) .01M

NO_2^-, .001M NO_3^-; (2).01M NO_2^-, .01M NO_3^-; and (3) .01M NO_3^-, .001M NO_2^-. The

samples were made and portions of these original samples were tested six times in the

presence of varying amounts of alumina. A percent error was calculated from the

determined concentrations of NO_3^- and NO_2^- with respect to the known concentrations in

each sample (1-3) and sample type with alumina present and absent in the sample solution.

The percent errors were calculated for each of the six measurements and the average

percent error for each sample was found. This is the percent error which is displayed in

Figures 3-1, 3-2, and 3-3. In essence, this percent error is a measure of how alumina

affects NO_x^- concentration measurements. From Figures 3-1, 3-2, and 3-3, it can be seen

that the presence of alumina in a sample solution does have an effect on the concentration

measurements.

Alumina in solution acts as a slightly basic buffer. Comparing two solutions of the

same NO_x^- ion concentrations, with one solution containing alumina and the other without,

the solution containing alumina requires a slight amount more acid than the solution

without alumina to acidify to a particular pH. Though the alumina itself does not
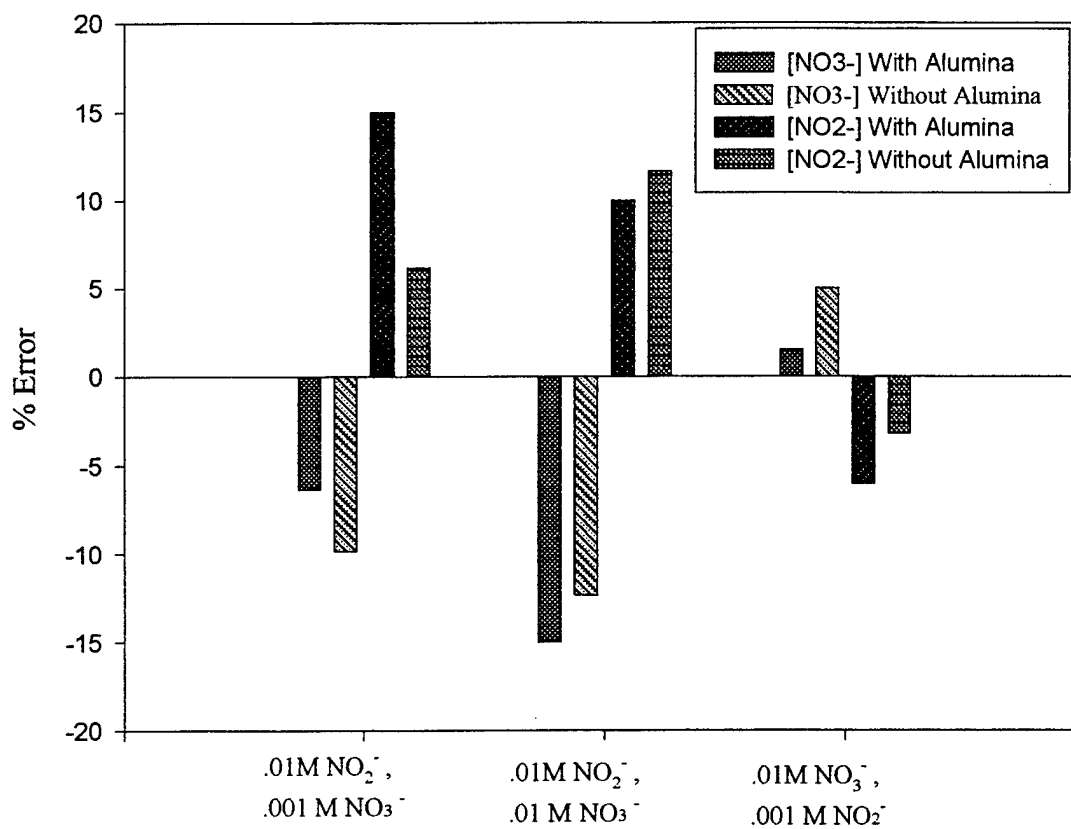
Figure 3-1. Average Percent Error in Repeated [NO3-] and [NO2-] Measurements for Three Different Untreated Samples of Known Concentrations With and Without Powderized Alumina Present
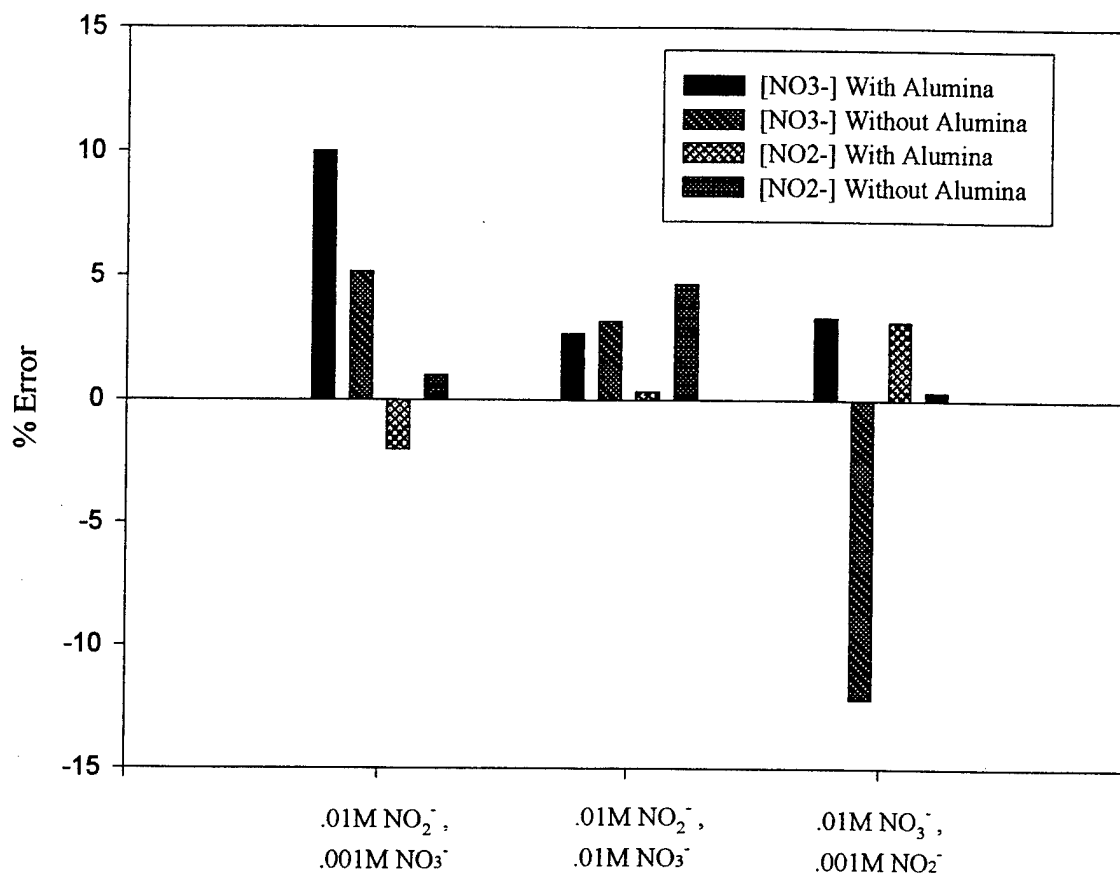
Figure 3-2. Average Percent Error in Repeated [NO3-] and [NO2-] Measurements for Three Different K2CO3-Treated Samples of Known Concentrations With and Without Treated Alumina Present
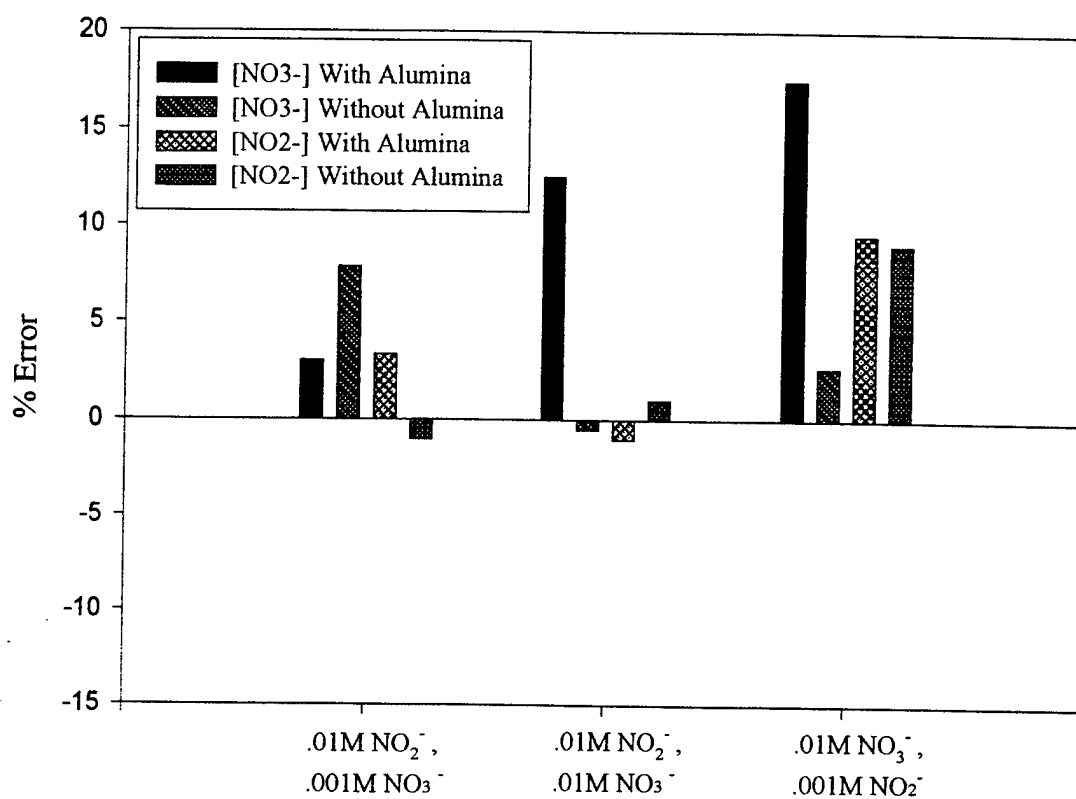
Figure 3-3. Average Percent Error in Repeated [NO3-] and [NO2-] Measurements for Three Different KOH-Treated Samples of Known Concentrations With and Without Treated Alumina Present

interfere with NO_x^- measurements, the extra acid which is required slightly increases the overall ionic strength of the sample. This may account for some of the disparity in the percent errors displayed for the same solutions with and without alumina in Figures 3-1, 3-2, and 3-3.

NO_x^- Percent Recovery

In order to ascertain the reliability of the aqueous testing method, surface NO_x^- quantities were correlated to gaseous input and output quantities of NO_x used in Max Lee's fixed reactor bed. Lee monitored input and output concentrations of NO_x gas over time in the reactor bed. When the total number of moles of output NO_x gas measured in the reactor bed are subtracted from the total moles of NO_x gas going into the reactor bed, the remaining amount should be the molar sum of the nitrate and nitrite which is formed on the alumina surface:

$$NOx_{(g)IN} - NOx_{(g)OUT} = NOx^-_{(s)SURFACE} \qquad (3-1)$$

The gaseous input/output data were correlated to the aqueous measurements in Figures 3-4, 3-5, and 3-6 for the three types of samples. In these figures, the ratio of $NO_2:NO$ gas in the feed gas were varied. From Figure 3-4, for untreated alumina, it can be seen that except for the 500:200 $NO_2:NO$ run, surface and gaseous data are in good agreement. In Figures 3-5 and 3-6, for the treated aluminas, the surface NO_x^- measurements are overestimated, particularly for runs where there was much more NO_2 than NO in the airstream. While the test method was usually accurate to within 20 percent, the overestimation of surface NO_x^- for the runs with the treated aluminas with less NO gas may be due to the less overall quantities of NO_x^- on these samples. In general, the test
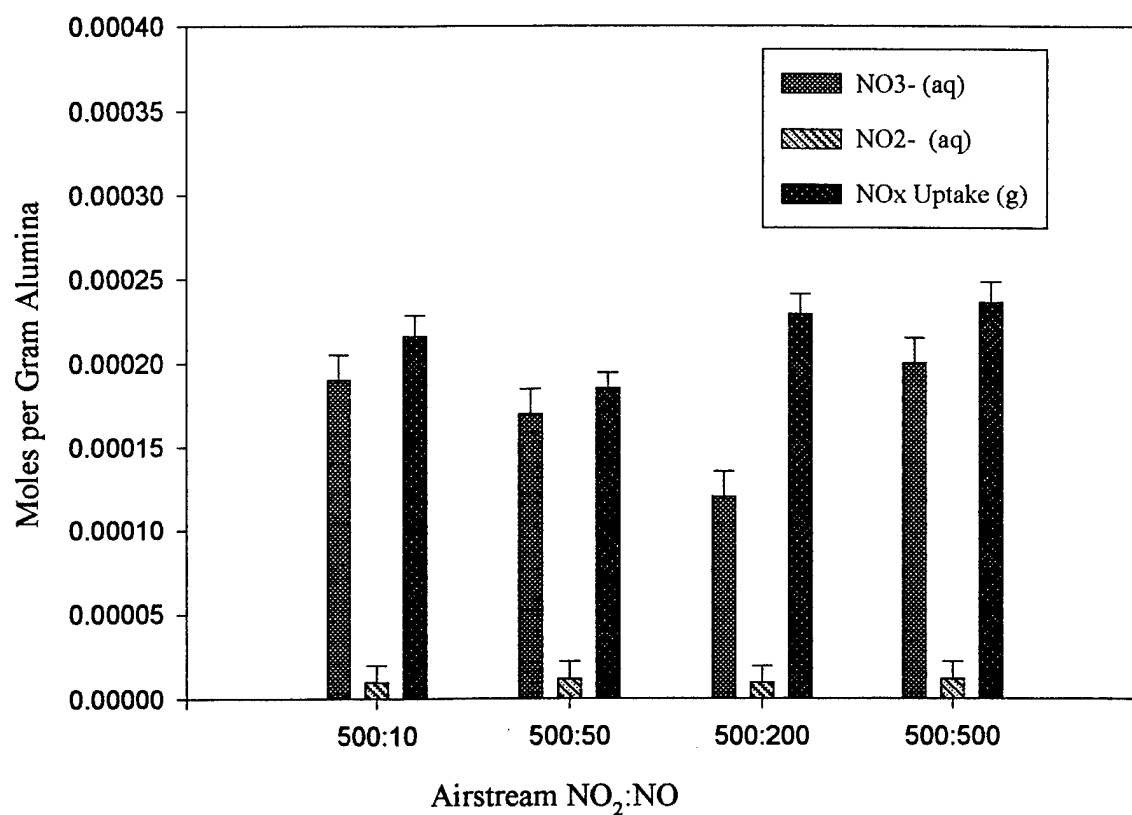
Figure 3-4. Moles Nitrate and Nitrite per Gram Alumina Determined by Aqueous ISE Measurement and Total NOx Uptake per Gram Alumina in the Reactor Bed for Untreated Alumina with Error Bars According to 2 Standard Deviations, 200C
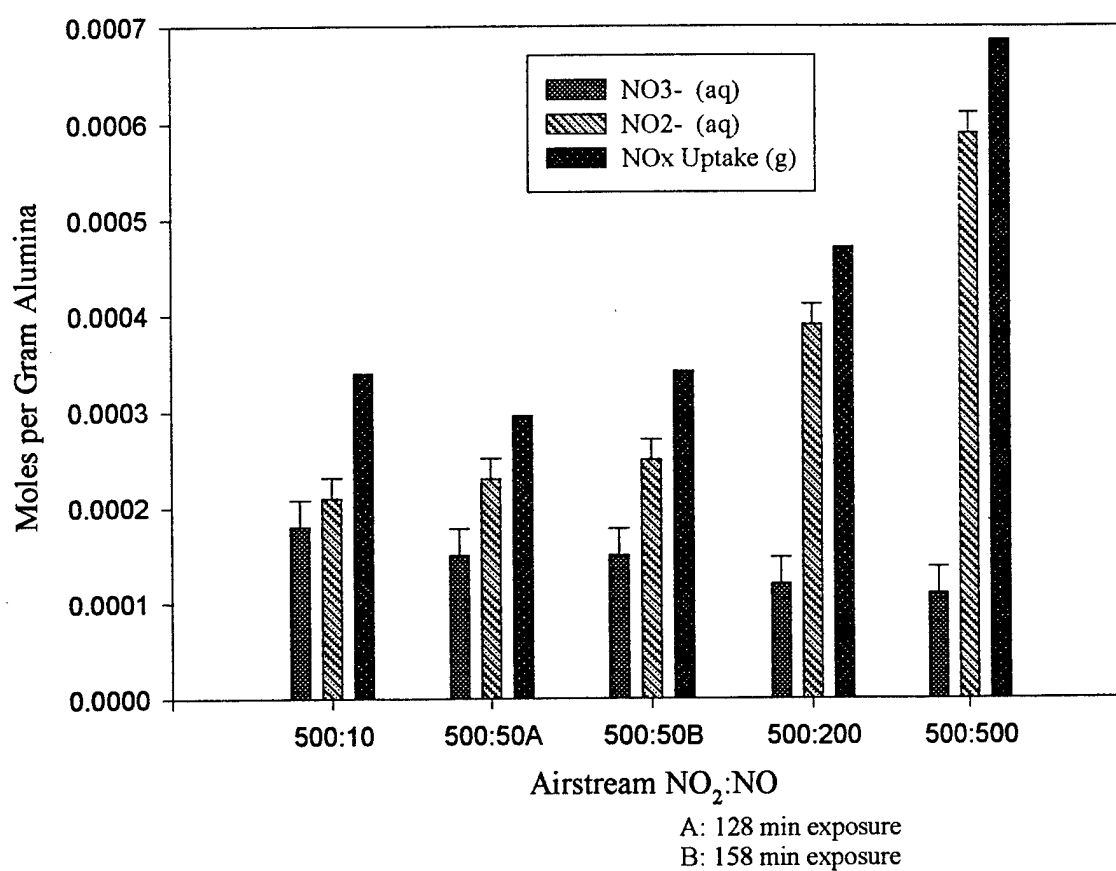
Figure 3-5. Moles Nitrate and Nitrite per Gram Alumina Determined by Aqueous ISE Measurement and Total NOx Uptake per Gram Alumina in the Reactor Bed for K2CO3-Treated Alumina with Error Bars According to 2 Standard Deviations, 200C
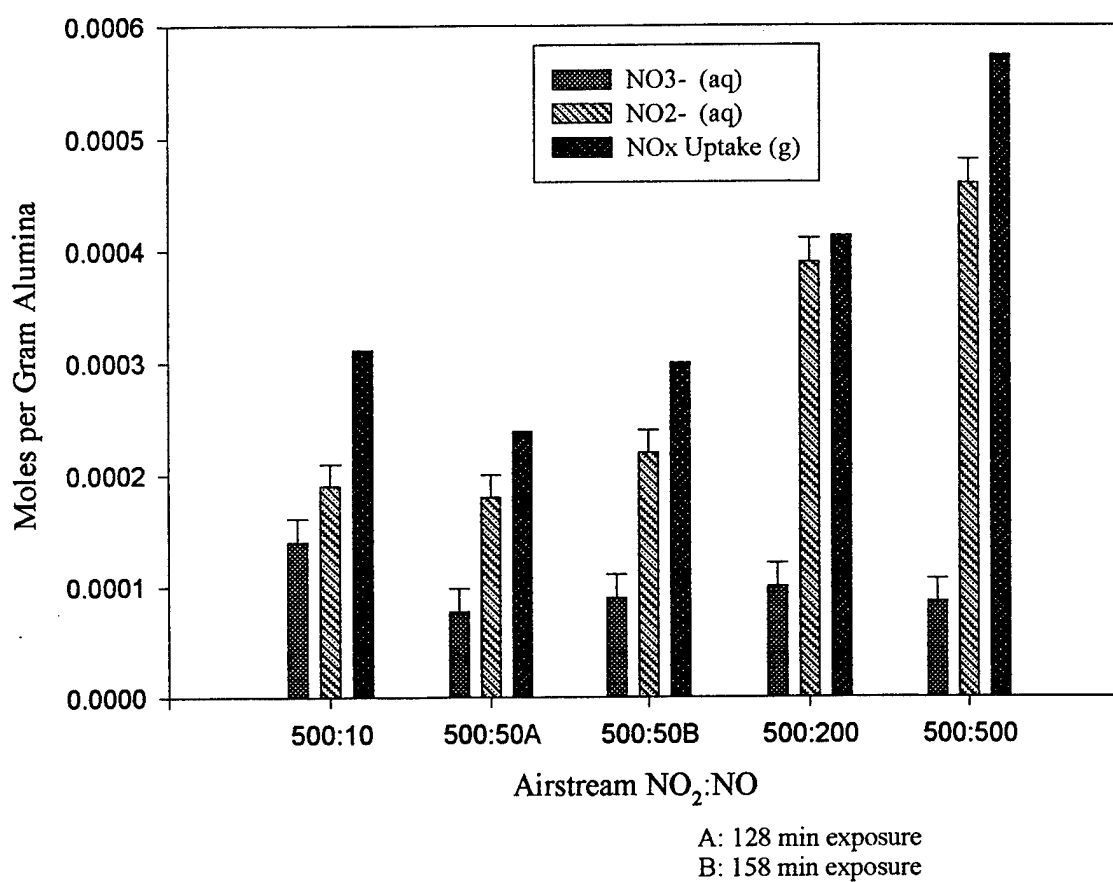
Figure 3-6. Moles Nitrate and Nitrite per Gram Alumina Determined by Aqueous ISE Measurement and Total NOx Uptake per Gram Alumina in the Reactor Bed for KOH-Treated Alumina with Error Bars According to 2 Standard Deviations, 200C

method overestimated surface NO_x^- quantities on treated materials, at times up to 20%. Additional information is provided in the 'Error Analysis' section.

Other Ion Interferences

Besides the interference of NO_2^- with NO_3^- measurements and vise-versa, several other anions may cause interferences in NOx^- ion measurements by the ISE method. Orion, the manufacturer of the ISEs used in this project, lists various anions which may cause possible interferences with measurements at certain concentrations (Orion Research, 1991). For the Orion model 93-07 nitrate electrode several anions are listed as interferences. Only a few of these were present in the samples tested: NO_2^-, CO_3^{-2}, and Cl^-. The nitrite interference was removed through the addition of sulfamic acid as described previously. Carbonate (assumed to be present as dissolved carbon dioxide was presumed to be present in latent DI water) was removed also by the addition of sulfamic acid, as at pH's below 4.5 carbonate is converted to carbon dioxide (Orion Research, 1991). Chloride ion was assumed to be present as the filling solution in the pH electrode contained 3M KCl solution. Due to the very low flow rate of this fill solution from the electrode to the sample solution (about 1 μL/hr) and the short time needed to obtain pH readings (less than 1 minute), chloride was not considered to be present at significant levels to cause any interference with NO_x^- ion measurement.

The interferences listed by Orion for the nitrite electrode (model 93-46 manual) and which may have been present in actual samples included nitrate, carbonate, sulfate, and chloride. It proved impossible to remove the nitrate interference for measurement by the ISE method. The nitrite measurement procedure was designed with this taken into

account so that nitrate was present in the standards and samples at equal levels.

Carbonate was removed by acidification using sulfuric acid. This addition of sulfuric acid

introduced sulfate ion into solution. The level of this ion was equalized in the standards

and samples by acidifying to a constant pH between 4.0 and 4.5. The chloride interference

was negligible for the same reasons mentioned previously.

Stability of Standard Solutions

The nitrate and nitrite standards used in the procedures described in the previous

chapter were stable over a period of about 12-15 hours. After this time period, changes in

cell potential were observed, on the order of 10-20% of the original mV reading after 24

hours. As a result, new standards were made each day of testing. Testing during a day

never exceeded 12 hours.

Test Method Characteristics

Calibration

Typical calibration curves for nitrate and nitrite, mV vs $[NO_x^-]$, are shown in

Figures 3-7 and 3-8, respectively. The linear range of both the nitrate and nitrite ISE's

was 1×10^{-4} M to .05 M. Five standard solutions were used in the calibration for both

nitrate and nitrite analyses: 1×10^{-4} M, 1×10^{-3} M, 5×10^{-3} M, 1×10^{-3} M, and 5×10^{-2} M.

These were prepared by successive serial dilutions of 0.1M nitrate or nitrite solutions

which were made by adding specific amounts of nitrate or nitrite compounds to a known

volume of DI water. There were small variations in the concentrations of the standard

solutions due to dilution as a result of the addition of components required to simulate
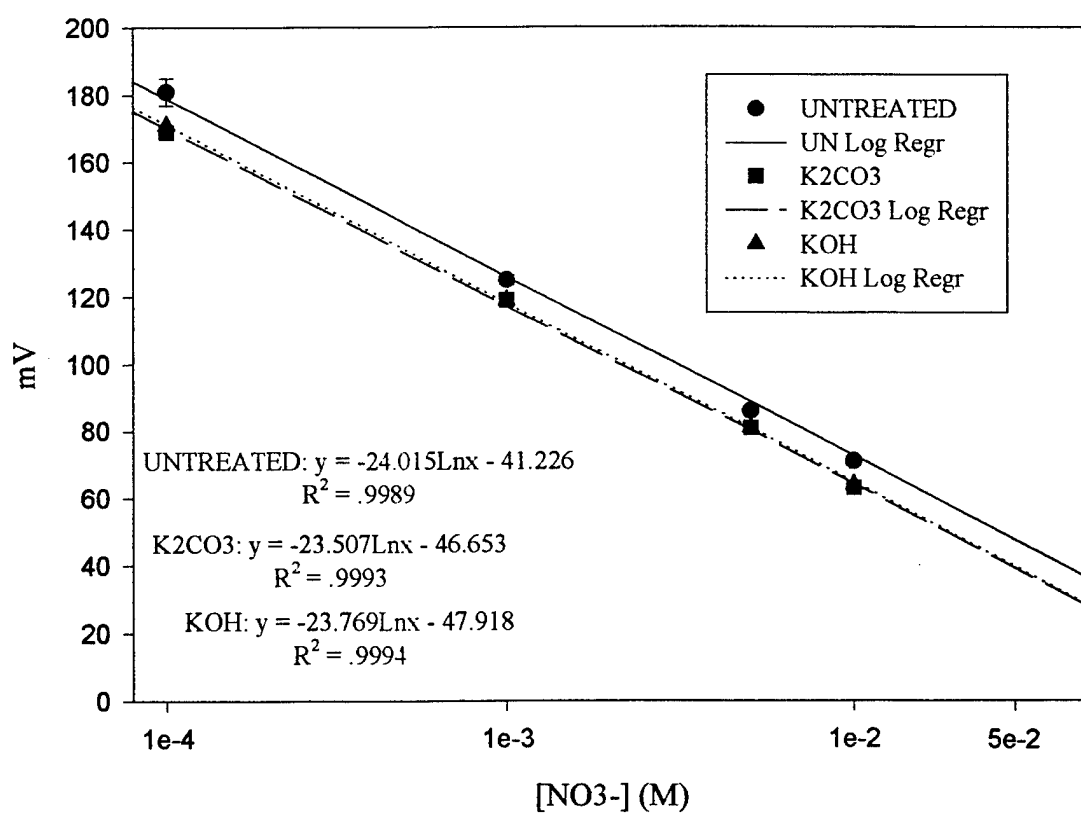
Figure 3-7. Typical Calibration Curves for Nitrate, mV vs. [NO3-], with Error Bars According to 2 Standard Deviations in Hourly mV Readings
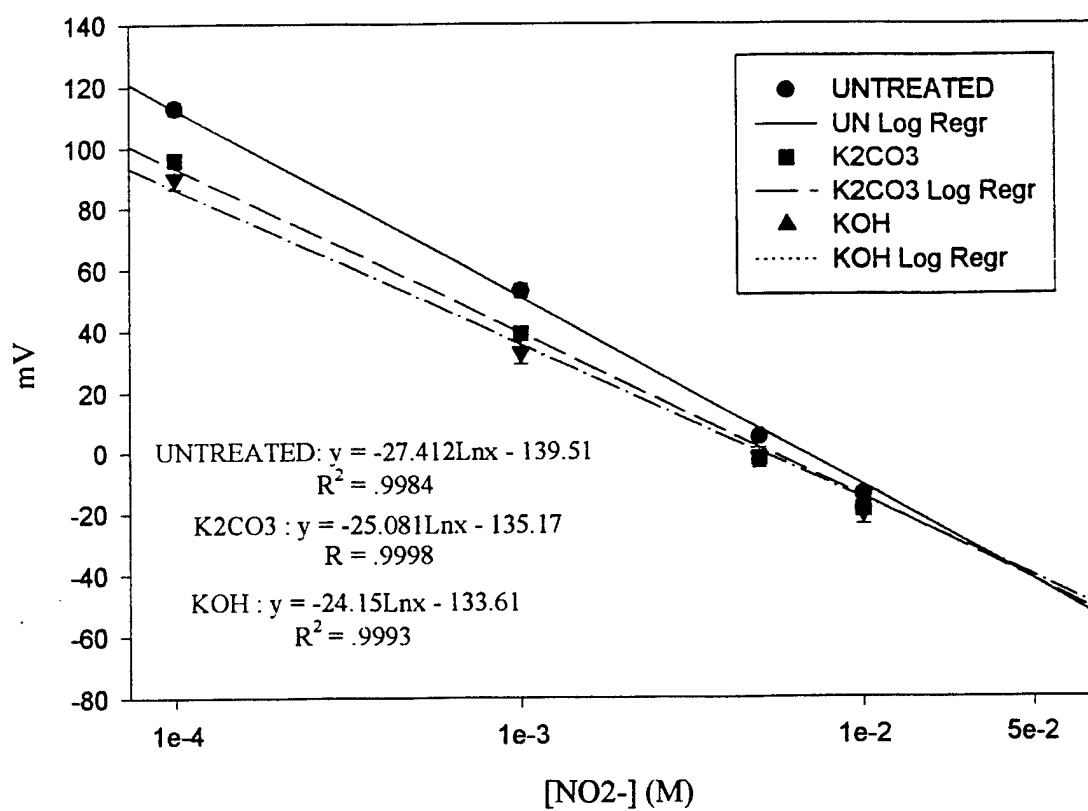
Figure 3-8. Typical Calibration Curves for Nitrite, mV vs. [NO2-], with Error Bars According to 2 Standard Deviations in Hourly mV Readings

typical sample compositions. The new standard concentrations were calculated through the re-measurement of the volume of the altered standards. The dilutions usually changed the standard concentration by less than 3%. Millivolt readings from the standard concentrations were used to determine a logarithmic calibration curve. The correlation coefficient values calculated for these log regression equations were typically greater than .998. At times, particularly for nitrite assays, 4-point calibrations were used as the removal of the highest calibration point from the regression often returned a higher R^2 value. If the standard with the .05M concentration was not diluted to a concentration around .04M, the regression suffered as .05M represents the upper linear range of the ISE. The removal of this calibration point was justified as the highest concentrations observed in this study did not exceed .015M.

Millivolt readings for standard solutions were stable over the duration of the testing day. During testing, the electrode may 'drift' over time, but this operational variation inherent in ISEs was minimal in this study. However, there was variation in mV measurements for standard solutions used for different days. In this way, variation in calibration values on a specific day (hourly basis) was minimal but daily variation was more significant. The daily variation was likely due to the varying temperature of the laboratory and the height of the fill solution in the reference electrode. The standard deviation in mV on a hourly and daily basis can be found in Table A-1 in the Appendix.

Limits of Detection

Limits of detection (LOD) were determined for $[NO_3^-]$ and $[NO_2^-]$ in varying sample matrices by using the standard deviations obtained when low-level measurements

were repeated. The concentration of the sample used was 5×10^{-5}M NO_3^- and 5×10^{-5} M NO_2^-. A large-volume sample was made with these concentrations and six fractions of the sample were tested for $[NO_3^-]$ and $[NO_2^-]$. The standard deviation in concentration was determined for these measurements and multiplied by a factor of three to obtain LOD values. This procedure was completed for the three sample treatments. The LODs determined for varying sample types (treatments) are shown below in Table 3-2. The LODs for the treated materials are higher than those of untreated. This is due to the greater deviation (less precision) inherent in the test method for treated materials (see 'Error Analysis').

Table 3-2. Method Limits of Detection for $[NO_x^-]$ (M).

	Untreated	K_2CO_3	KOH
NO_3^-	1.0E-05	1.4E-05	1.5E-05
NO_2^-	2.4E-05	5.0E-05	5.5E-05

The Orion ISE manuals list LOD values for $[NO_3^-]$ and $[NO_2^-]$ as 1×10^{-6} M and 4×10^{-5} M, respectively. The LOD values for nitrite determined experimentally here and listed in the Orion Nitrite ISE Manual are similar. The experimental LOD for nitrate was higher than that listed in the Orion Nitrate ISE Manual. At nitrate concentrations less than 6×10^{-5}M, the calibration curve appears to plateau and concentrations below the experimentally determined LOD could not be distinguished from background noise. In actual sample testing, the amount of alumina and volume of DI water in the sample

solutions was manipulated to ensure that the measured NO_x^- concentrations were within the linear range of the ISEs and above the method LODs. This was done qualitatively after information pertaining to the degree of NO_x exposure was obtained from Max Lee.

Error Analysis: ISE Method

After many samples with known NO_2^- and NO_3^- (NO_x^-) concentrations were tested, it was observed that there was a consistent error in NO_x^- concentration measurements. In order to estimate the error inherent in the testing method an error analysis was performed on samples of varying treatments and concentrations. The approach was to classify samples based on treatment type and relative NO_x^- concentrations and apply the case-specific error bars (and/or any correction factors) to samples based on their classification. Sample concentrations were classified into six configurations which represented typically observed concentrations in tested samples. These six samples, referred to as 'ERR' samples are subdivided according to treatment type. These ERR samples were made to simulate different treatment matrices by adding the specific treated (unexposed) alumina to the solutions. In effect, the only difference between actual, exposed samples which were tested and the ERR samples was the path in which the NO_x^- compounds were introduced into solution; by exposure to NO_x gas in the reactor bed for actual samples and by addition of known amounts of NO_x^--containing compounds into the ERR samples. The ERR samples were tested and re-tested six times for each of the three sample treatment types. Based on the repeated measurements, important statistical variables were calculated for concentration measurements including the mean, standard deviation (SD), median, and the range. Correction factors (CF) were calculated based on the average percent errors

observed. The 95% confidence interval (two standard deviations) for concentration was also included. In all, thirty-six different values of these variables were calculated from these measurements (6 sample concentrations types times 3 sample treatment types for both nitrate and nitrite). These variables, along with the six concentration measurements for each sample category are listed in Table 3-3.

Mean

The experimental means and the associated percent error from the known concentrations listed in Table 3-3 indicate the degree of accuracy of the test method for various sample matrices. For nitrite the range of percent error observed throughout Table 3-3 is -13% to 23%. For nitrate the range is -17% to 27% error. The higher percent errors are observed in ERR1, ERR2, and ERR3 which all have the lowest nitrate concentration of .0001M. For ERR4, ERR5, and ERR6, which have higher nitrate concentrations, the percent errors observed are lower. Through the mean and percent error observations, the systematic error of the test method can be estimated.

Nitrate

For most of the 6 ERR samples, the highest error in nitrate measurement is observed with KOH-treated alumina. Alumina treated with K_2CO_3 also produced high nitrate measurements, but these were usually less than those of the KOH-treated alumina. These high measurements may be due to factors concerning the ionic strengths of these sample types. These two compounds are strong bases, with KOH being the stronger of the two. Compared to an untreated sample, a sample treated with one of these strong

Table 3-3. Measured [NO3-] and [NO2-] for Solutions of Known NOx Concentrations for Use in Error Analysis. Alumina Present

ERR1 = .0001M NO2-, .0001M NO3-

ERR1 Untreated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	8.4E-05	7.6E-05	7.7E-05	8.3E-05	9.7E-05	8.0E-05	8.3E-05	7.6E-06	8.2E-05	7.6E-05	9.7E-05	-17.2	1.2	1.5E-05
[NO2-]	1.0E-04	1.0E-04	9.4E-05	8.7E-05	9.6E-05	1.0E-04	9.6E-05	5.2E-06	9.8E-05	8.7E-05	1.0E-04	-3.8	1.0	1.1E-05

ERR1 K2CO3-Treated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	1.30E-04	1.4E-04	1.2E-04	1.3E-04	1.0E-04	1.0E-04	1.2E-04	1.7E-05	1.3E-04	1.0E-04	1.4E-04	20	0.83	3.3E-05
[NO2-]	0.00011	1.0E-04	1.0E-04	1.1E-04	1.0E-04	1.2E-04	1.1E-04	8.2E-06	1.1E-04	1.0E-04	1.2E-04	6.7	0.94	1.6E-05

ERR1 KOH-Treated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	1.3E-04	1.2E-04	1.1E-04	1.2E-04	1.2E-04	1.4E-04	1.2E-04	1.0E-05	1.2E-04	1.1E-04	1.4E-04	23.3	0.81	2.1E-05
[NO2-]	1.2E-04	1.1E-04	1.3E-04	1.2E-04	1.4E-04	1.2E-04	1.2E-04	1.0E-05	1.2E-04	1.1E-04	1.4E-04	23.3	0.81	2.1E-05

ERR2 = .0005M NO2-, .0001M NO3-

ERR2 Untreated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	1.2E-04	1.2E-04	9.2E-05	9.3E-05	9.8E-05	1.0E-04	1.0E-04	1.3E-05	9.9E-05	9.2E-05	1.2E-04	3.8	0.96	2.6E-05
[NO2-]	4.3E-04	4.7E-04	4.9E-04	4.2E-04	3.9E-04	4.2E-04	4.4E-04	3.7E-05	4.3E-04	3.9E-04	4.9E-04	-12.7	1.1	7.3E-05

ERR2 K2CO3-Treated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	1.1E-04	1.2E-04	1.1E-04	1.0E-04	1.3E-04	1.2E-04	1.2E-04	1.0E-05	1.2E-04	1.0E-04	1.3E-04	15.0	0.87	2.1E-05
[NO2-]	5.3E-04	5.1E-04	5.0E-04	5.2E-04	5.1E-04	4.9E-04	5.1E-04	1.4E-05	5.1E-04	4.9E-04	5.3E-04	2.0	0.98	2.8E-05

ERR2 KOH-Treated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	1.2E-04	1.0E-04	1.1E-04	1.5E-04	1.3E-04	1.2E-04	1.2E-04	1.7E-05	1.2E-04	1.0E-04	1.5E-04	21.7	0.82	3.4E-05
[NO2-]	4.9E-04	5.3E-04	5.1E-04	5.3E-04	5.7E-04	5.3E-04	5.3E-04	2.7E-05	5.3E-04	4.9E-04	5.7E-04	5.3	0.95	5.3E-05

ERR3 = .001M NO2-, .0001M NO3-

ERR3 Untreated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	1.4E-04	1.2E-04	1.3E-04	1.2E-04	1.1E-04	1.1E-04	1.2E-04	1.2E-05	1.2E-04	1.1E-04	1.4E-04	21.7	0.82	2.3E-05
[NO2-]	1.0E-03	9.5E-04	9.6E-04	9.1E-04	9.2E-04	9.1E-04	9.4E-04	3.5E-05	9.4E-04	9.1E-04	1.0E-03	-5.8	1.1	7.1E-05

ERR3 K2CO3-Treated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	1.1E-04	1.0E-04	1.2E-04	1.2E-04	1.4E-04	1.3E-04	1.2E-04	1.4E-05	1.2E-04	1.0E-04	1.4E-04	20.0	0.83	2.8E-05
[NO2-]	1.1E-03	1.1E-03	1.2E-03	1.1E-03	1.1E-03	1.0E-03	1.1E-03	6.3E-05	1.1E-03	1.0E-03	1.2E-03	10.0	0.91	1.3E-04

ERR3 KOH-Treated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	1.3E-04	1.2E-04	1.3E-04	1.5E-04	1.1E-04	1.2E-04	1.3E-04	1.4E-05	1.3E-04	1.1E-04	1.5E-04	26.7	0.79	2.7E-05
[NO2-]	1.1E-03	1.1E-03	1.2E-03	1.0E-03	1.1E-03	1.1E-03	1.1E-03	6.3E-05	1.1E-03	1.0E-03	1.2E-03	10.0	0.91	1.3E-04

ERR4 = .0001M NO2-, .0005M NO3-

ERR4 Untreated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	5.4E-04	5.2E-04	4.9E-04	5.1E-04	5.0E-04	5.1E-04	5.1E-04	1.7E-05	5.1E-04	4.9E-04	5.4E-04	2.3	0.98	3.4E-05
[NO2-]	9.8E-05	1.0E-04	9.7E-05	9.5E-05	9.6E-05	9.8E-05	9.7E-05	1.8E-06	9.8E-05	9.5E-05	1.0E-04	-2.7	1.0	3.5E-06

ERR4 K2CO3-Treated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	5.5E-04	5.2E-04	5.0E-04	5.3E-04	4.9E-04	5.4E-04	5.2E-04	2.3E-05	5.3E-04	4.9E-04	5.5E-04	4.3	0.96	4.6E-05
[NO2-]	1.1E-04	1.2E-04	9.8E-05	1.2E-04	1.0E-04	1.1E-04	1.1E-04	9.4E-06	1.1E-04	9.8E-05	1.2E-04	9.7	0.91	1.9E-05

ERR4 KOH-Treated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	6.0E-04	5.2E-04	5.7E-04	5.3E-04	5.4E-04	5.2E-04	5.5E-04	3.2E-05	5.4E-04	5.2E-04	6.0E-04	9.3	0.91	6.4E-05
[NO2-]	1.0E-04	1.1E-04	1.1E-04	1.2E-04	9.8E-05	1.0E-04	1.1E-04	8.5E-06	1.1E-04	9.8E-05	1.2E-04	6.3	0.94	1.7E-05

ERR5 = .0001M NO2-, .001M NO3-

ERR5 Untreated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	9.6E-04	9.8E-04	1.0E-03	1.1E-03	9.9E-04	1.0E-03	1.0E-03	4.9E-05	1.0E-03	9.6E-04	1.1E-03	0.5	1.0	9.8E-05
[NO2-]	1.1E-04	8.9E-05	9.0E-05	9.2E-05	8.5E-05	9.0E-05	9.3E-05	8.8E-06	9.0E-05	8.5E-05	1.1E-04	-7.3	1.1	1.8E-05

ERR5 K2CO3-Treated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	1.1E-03	1.0E-03	1.0E-03	1.2E-03	1.1E-03	1.2E-03	1.1E-03	8.9E-05	1.1E-03	1.0E-03	1.2E-03	10.0	0.91	1.8E-04
[NO2-]	1.1E-04	9.0E-05	8.9E-05	1.1E-04	1.1E-04	1.1E-04	1.0E-04	1.1E-05	1.1E-04	8.9E-05	1.1E-04	3.2	0.97	2.1E-05

ERR5 KOH-Treated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	1.4E-03	1.1E-03	1.2E-03	1.1E-03	1.0E-03	1.1E-03	1.2E-03	1.4E-04	1.1E-03	1.0E-03	1.4E-03	15.0	0.87	2.8E-04
[NO2-]	9.9E-05	1.0E-04	9.6E-05	1.0E-04	1.1E-04	1.0E-04	1.0E-04	4.8E-06	1.0E-04	9.6E-05	1.1E-04	0.83	0.99	9.5E-06

ERR6 = .001M NO2-, .001M NO3-

ERR6 Untreated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	9.2E-04	9.8E-04	9.2E-04	1.1E-03	1.1E-03	1.0E-03	1.0E-03	8.1E-05	9.9E-04	9.2E-04	1.1E-03	0.3	1.0	1.6E-04
[NO2-]	8.0E-04	9.3E-04	9.1E-04	8.5E-04	9.1E-04	9.0E-04	8.8E-04	4.9E-05	9.1E-04	8.0E-04	9.3E-04	-11.7	1.1	9.8E-05

ERR6 K2CO3-Treated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	1.1E-03	1.1E-03	1.0E-03	1.2E-03	1.1E-03	1.2E-03	1.1E-03	7.5E-05	1.1E-03	1.0E-03	1.2E-03	11.7	0.90	1.5E-04
[NO2-]	1.1E-03	1.1E-03	1.1E-03	1.0E-03	1.1E-03	1.0E-03	1.1E-03	5.5E-05	1.1E-03	1.0E-03	1.1E-03	5.0	0.95	1.1E-04

ERR6 KOH-Treated Samples (Alumina Present)

	1	2	3	4	5	6	Mean	SD	Median	Min Value	Max Value	% Err	CF	95% CI (2SD)
[NO3-]	1.1E-03	9.7E-04	1.0E-03	1.1E-03	1.1E-03	1.0E-03	1.0E-03	6.1E-05	1.1E-03	9.7E-04	1.1E-03	4.5	0.96	1.2E-04
[NO2-]	9.7E-04	9.8E-04	9.9E-04	1.0E-03	9.9E-04	1.1E-03	1.0E-03	4.8E-05	9.9E-04	9.7E-04	1.1E-03	0.5	1.0	9.5E-05

bases requires more sulfamic acid to acidify to a certain pH. Also, very little nitrite is found in untreated samples whereas this species is present in much greater quantities in treated samples (see the following sections). More nitrite also requires additional sulfamic acid as any reaction which is observed during the addition of the sulfamic acid warrants continuous addition of acid until the reaction is complete. A solution of the particular base compound (K_2CO_3 or KOH) was added to bring the pH back up to 2.5. Due to these additions of additional sulfamic acid and additional base solution to the sample, the sample will have a higher ionic strength than the standards which are used in the calibration. In effect, the necessary addition of these compounds, which allow for the measurement of nitrate, indirectly interfere with the measurement itself. The ERR3 sample is worth mentioning here as it shows the highest percent errors for nitrate measurement on the chart. Also note that the percent error for the untreated sample was 22% which is similar to the percent errors observed for the base treatments. This high error in the untreated ERR3 sample, compared to all other samples which have much lower percent errors, can be explained by the presence of nitrite. Since ERR3 contains the highest nitrite concentration, compared to ERR1 and ERR2, additional sulfamic acid was needed in the ERR3 sample. This situation is true for all three sample treatments, and hence, the untreated ERR3 also exhibits a large degree of error. Percent errors for nitrate measurements are lower in ERR samples 4, 5, and 6 as these samples contain greater amounts of nitrate.

Nitrite

The largest percent errors in nitrite measurement are also observed in ERR samples 1, 2, and 3. Accuracy in nitrite measurements varied by treatment type. For untreated alumina, nitrite measurement was underestimated in all 6 ERR samples as shown by the negative percent errors in Table 3-3. For treated alumina, nitrite measurements were usually within 10% of the known value. The lowest percent errors in nitrite measurement are observed in ERR6 which contains the highest nitrite (and nitrate) concentration. Overall, nitrite concentration measurements appeared to be slightly more accurate than those for nitrate.

Standard Deviation, Precision, and Random Error

The standard deviation values listed in Table 3-3 are fairly low. An unexpected observation is the fact that the deviations were of similar order for low and high concentrations. In fact, comparing the standard deviation of ERR1 with ERR6, the deviations in ERR1, which is ten times less the concentration of ERR6, are actually lower than for ERR6. Similar results were reported by Morie et al., (1972) who quantified nitrate using the older model of the Orion nitrate ISE. Most of the standard deviation values observed are on the order of 10^{-5}. The standard deviations reflect the reproducibility of the test methods, which can be characterized as precise to a large degree over the linear range of the ISEs as values. Comparing the standard deviation values for ERR1 and ERR6, the deviations in ERR6 are close to ten times higher than those of ERR1. This is due to the concentrations of ERR6 being ten times greater than those of ERR1. However, the standard deviations for ERR6 are a similar percent of concentration

as in ERR1. To examine the precision of the test methods for the various sample matrices, standard deviation may be expressed as a percent of concentration for each of the materials. This data is shown in Figures 3-9 and 3-10 for nitrate and nitrite measurements on the three materials, respectively. From Figures 3-9 and 3-10 the measurements for ERR6 are found to be slightly more precise than those of ERR1. The nitrite method was more precise than that for nitrate as values in Figure 3-10 for nitrite are less than those for nitrate in Figure 3-9. The average value of all data in Figure 3-10 was 6% whereas in Figure 3-9, this value was 10%.

Correction Factors, Accuracy and Systematic Error

For actual tested (exposed) samples, the sample was classified into one of the eighteen sample characterizations listed in Table 3-3 based on the experimentally determined aqueous NO_x^- concentrations. The determined NO_x^- concentrations were multiplied by the correction factors as the actual concentration. In data charts which are presented in the following section these corrected valued are presented. Error bars in these charts are the 95% confidence intervals calculated for each sample type listed in Table 3-3.

Results of Exposed Alumina Testing

In this section results are presented for the three sample types under varying conditions of exposure to NO_2 and NO gas in the reactor bed. The NO_x^- concentrations measured on the alumina surface varied according to sample type (treatment) and exposure time (NO_x gas volume). On untreated alumina, nitrate was present in greater

51
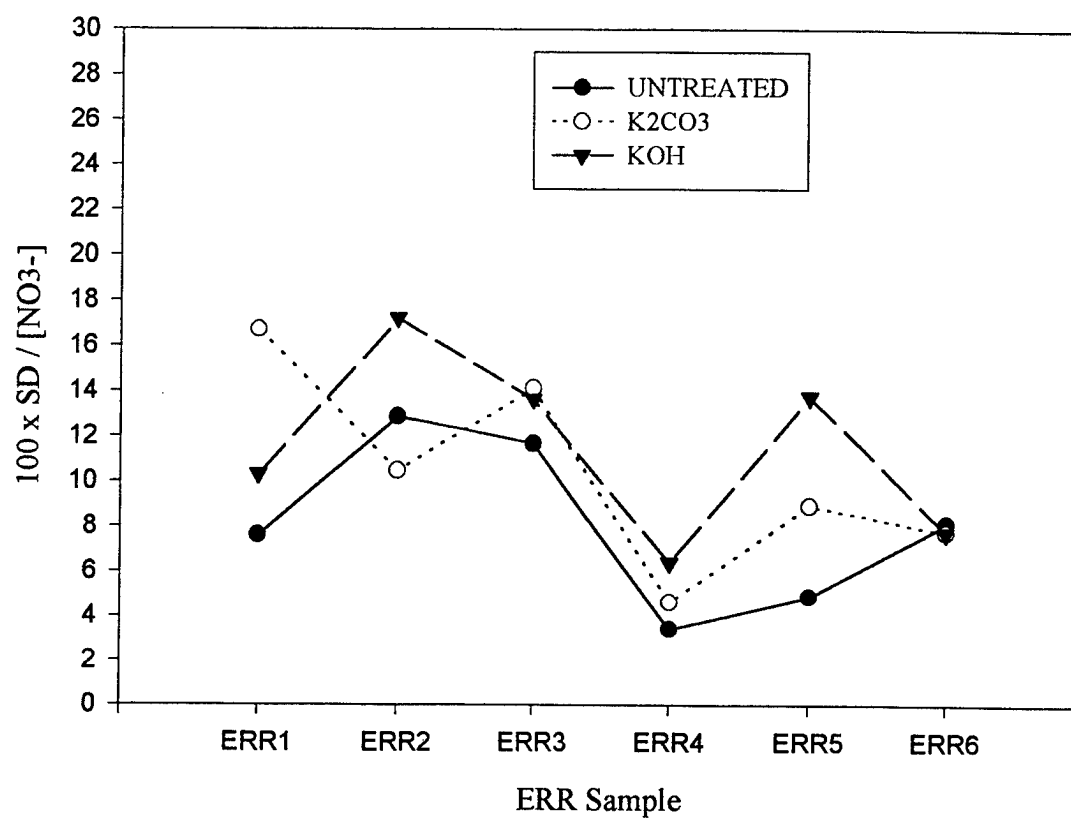
Figure 3-9. Standard Deviation in [NO3-] as a Percent of [NO3-]
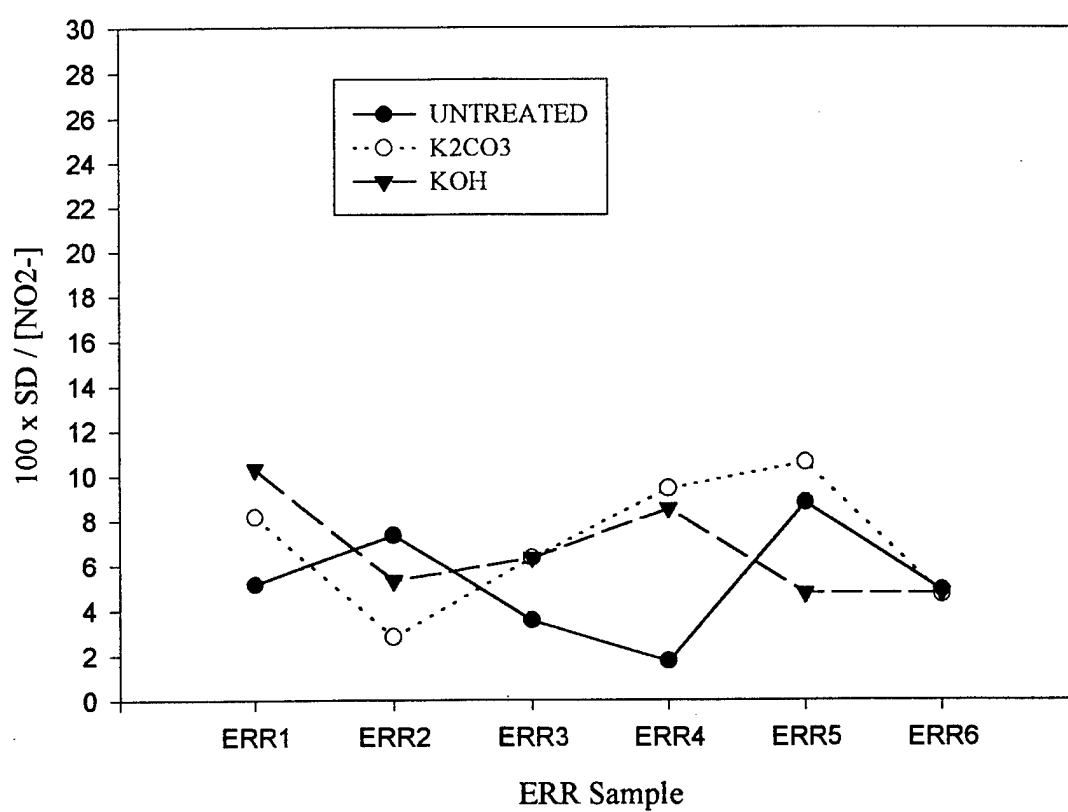
Figure 3-10. Standard Deviation in [NO2-] as a Percent of [NO2-]

amounts than nitrite, which was present but at low levels. On K_2CO_3-treated and KOH-treated alumina, nitrate and nitrite species were both present in higher quantities than on untreated alumina. This is consistent with the finding by Lee (1998) and Lee et al. (1998a and 1998b) that NO_x gas adsorption is enhanced by coating alumina with either K_2CO_3 or KOH.

Longbed Series

While many samples were tested during this investigation, results discussed here will be focused on measurements made on alumina samples taken from identical runs in the reactor bed. A brief description of these runs, directed by Max Lee, is presented here. The stationary reactor bed system is comprised of three separate adsorption chambers (stainless steel cylinders). For these specific runs, referred to as the 'longbed series', the alumina beds consisted of 15 grams of sorbent which were divided into 5, 3-gram layers. Each cylinder contained one bed (15g) which allowed for 3 beds to be exposed during one run. The three beds each contained one of the three alumina types discussed in these studies. Runs were made for 30, 60, 90, and 120 minute exposures for which the simulated flue gas consisted mostly of NO_2 gas (1950 ppm NO_2) with a trace of NO present (between 5-10 ppm NO). Input and output of NO_x through the bed was monitored continuously. Consequently, 20 samples of each sample treatment were obtained—5 bed sections (3g layers) exposed for 4 different times. In all, 60 samples were obtained, 20 from each alumina treatment. The longbed series is used here as it was designed to represent, on a smaller scale, how an actual alumina adsorbent filter bed might work and how the surface NO_x^- concentrations are distributed over time in different

sections of the bed. A detailed description of the actual reactor bed system operated by Max Lee can be found in Lee (1998) and Lee et al. (1998a or 1998b). The results from the longbed series are discussed according to sample type. Bed temperature for this series was 25°C.

Sorbent pH

The pH of the NO_x-exposed alumina sorbents was dependent on the treatment compound. For untreated alumina samples, the pH ranged from 4.0 to 5.5. For K_2CO_3-treated alumina, the pH ranged from 10.0 to 11.0. The pH range of KOH-treated alumina was 11.0 to 12.0. The nitrate concentration of the sample had a small effect on pH such that higher nitrate concentrations caused the pH to be towards the lower end of the stated ranges. Values of pH are plotted versus nitrate concentrations in Figure 3-11 for the longbed series. As shown in Figure 3-11, there is little variation in pH due to nitrate for each type of sorbent.

The alumina used in this study (Engelhard, Elyira, OH) had a pH of 5.7 when in aqueous solution. Several types of alumina which vary by pH are available from different manufacturers. Acidic, neutral, and basic aluminas obtained from Fisher Scientific had pH values of 4.4, 7.2, and 9.8, respectively, when in aqueous solution. Lee (1998) concluded that there was no difference in NO_x sorption for these materials (untreated).

Untreated alumina

The results from the longbed runs for the four different exposure times are
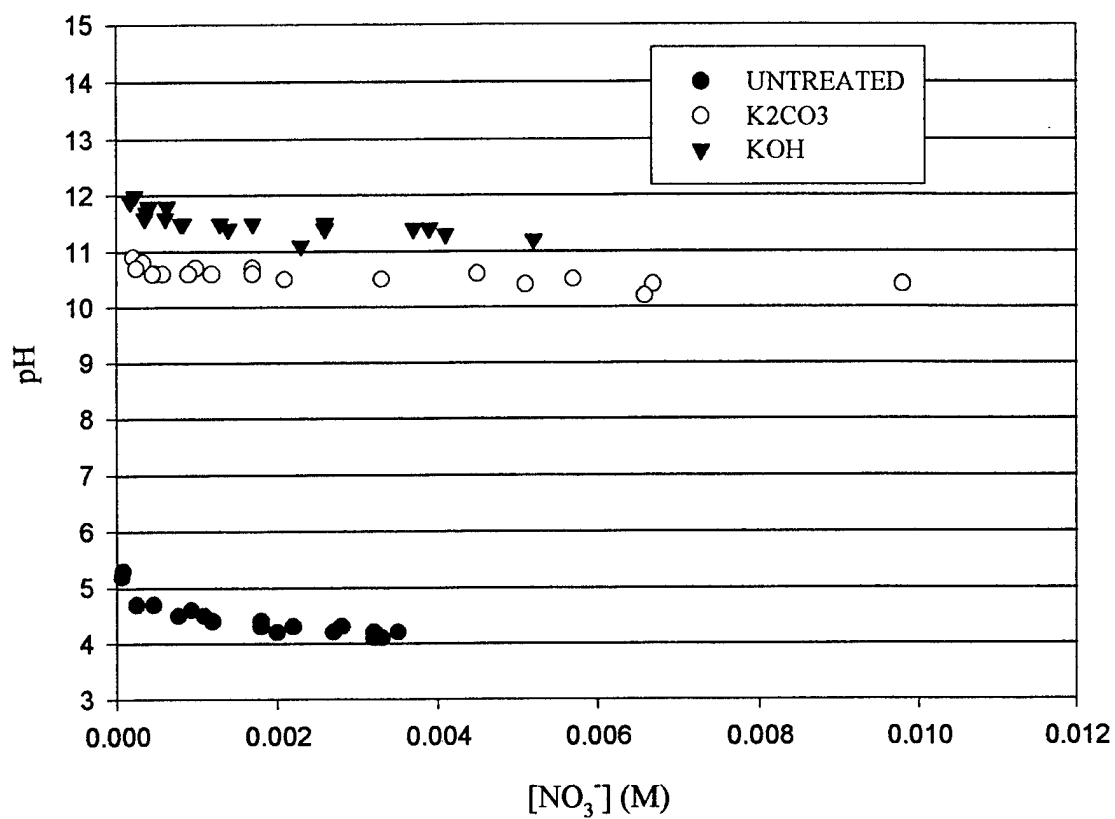
Figure 3-11. Sorbent pH vs. Nitrate Concentration

presented in Figures 3-12, 3-13, 3-14, and 3-15. Note that since concentration is subject

to the volume of solvent (DI water) and the weight of solute (alumina) in solution, the

concentrations have been converted to moles NO_x^- per gram alumina by multiplying the

concentration (M) by the solution volume (L) and dividing by the sorbent weight (g). The

data presented in this section will appear in this manner. The five bed sections (layers)

each consisted of 3g of alumina. The top of the bed was layer 1 while the bottom was

layer 5. Layer 1 was the most exposed as the gas flowed down from top to bottom in the

adsorbent bed. As expected for each time exposure, layer 1 shows the most NO_x^- present

while layer 5 shows the least.

Nitrate levels are much higher than nitrite on the surface of exposed untreated

alumina. The reasons for this difference may pertain to the instability of the aluminum

nitrite formed on the alumina surface, which is substantiated by enhanced NO formation in

the system (more on this later). The typical pH of an untreated alumina sample solution

varied from 4 to 5. Since nitrites are generally more unstable than nitrates and are easily

oxidized, presumably, any aluminum nitrite which is formed on the alumina surface may

quickly react with incoming NO_2 gas to form aluminum nitrate and NO. This process is

discussed in more detail in the following sections.

K₂CO₃-treated alumina

The surface NO_x^- from the four different exposure times for K_2CO_3-treated

alumina are shown in Figures 3-16, 3-17, 3-18, and 3-19. By comparing the data in

Figures 3-12 through 3-15 from the untreated alumina runs with those for the K_2CO_3-

treated alumina (3-16 through 3-19), it can be seen that much more NO_x^- is present on the

Figure 3-12 . Moles Nitrate and Nitrite per Gram Alumina for Sections of the Reactor Bed with Untreated Alumina, 30 min Exposure, Error Bars According to 2 Standard Deviations
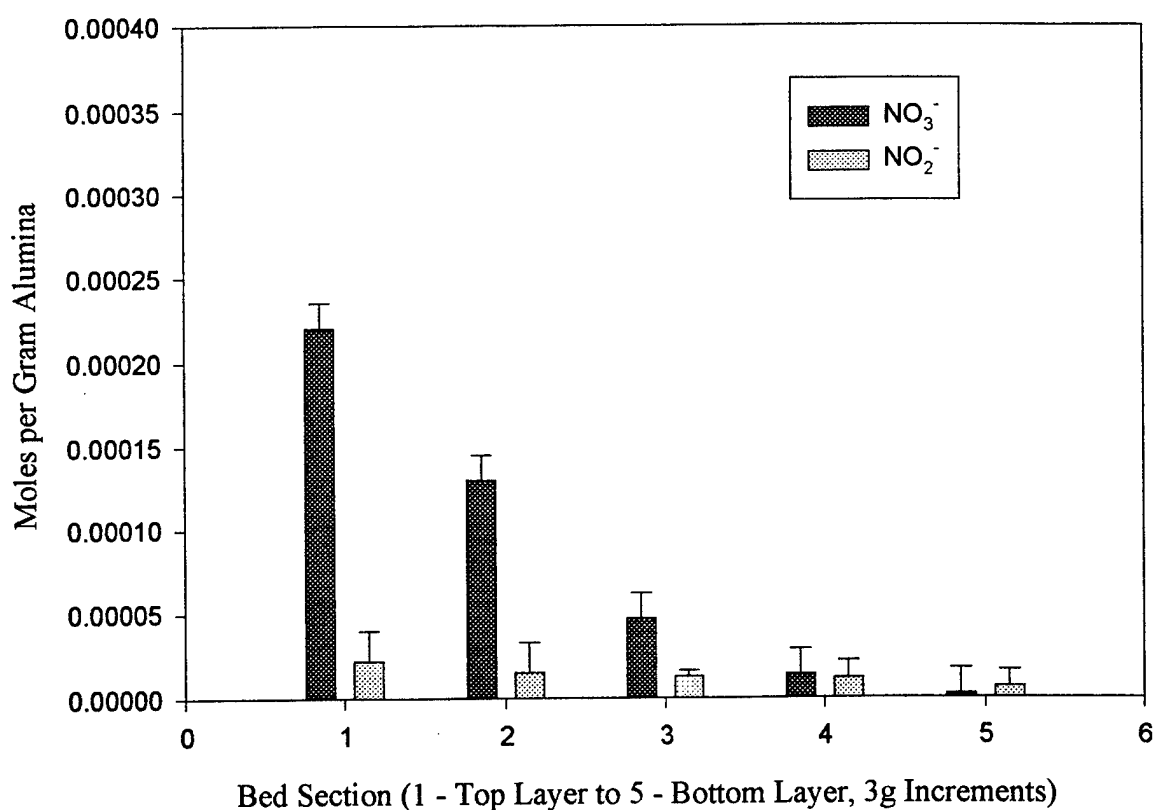
Figure 3-13. Moles Nitrate and Nitrite per Gram Alumina for Sections of the Reactor Bed with Untreated Alumina, 60 min Exposure, Error Bars According to 2 Standard Deviations
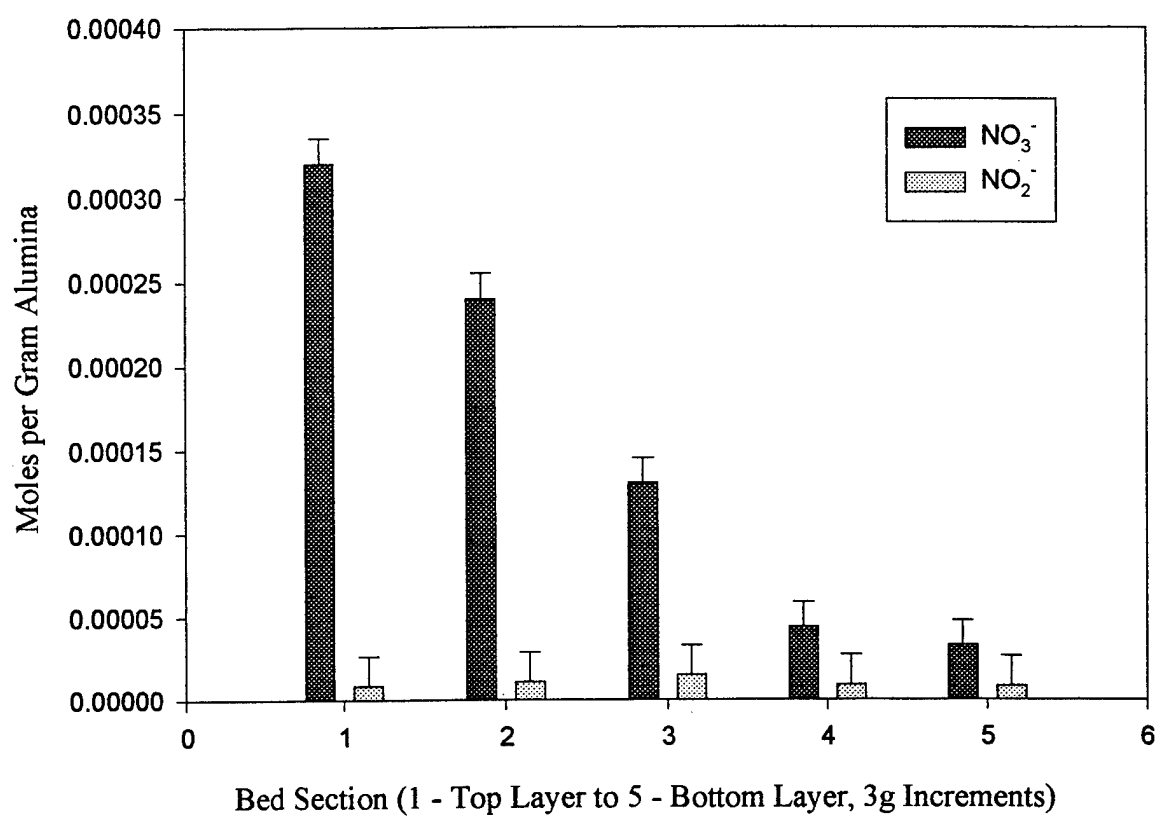
Figure 3-14. Moles Nitrate and Nitrite per Gram Alumina for Sections of the Reactor Bed with Untreated Alumina, 90 min Exposure, Error Bars According to 2 Standard Deviations
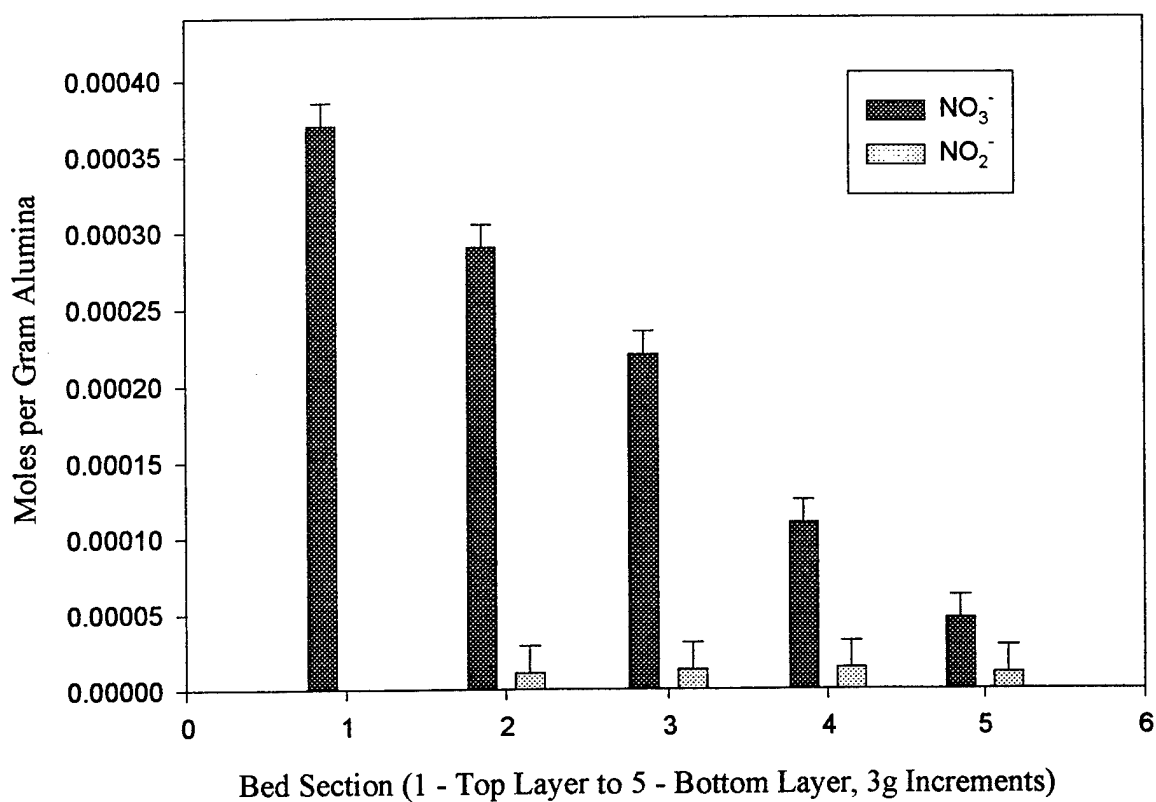
Figure 3-15. Moles Nitrate and Nitrite per Gram Alumina for Sections of the Reactor Bed with Untreated Alumina, 120 min Exposure, Error Bars According to 2 Standard Deviations
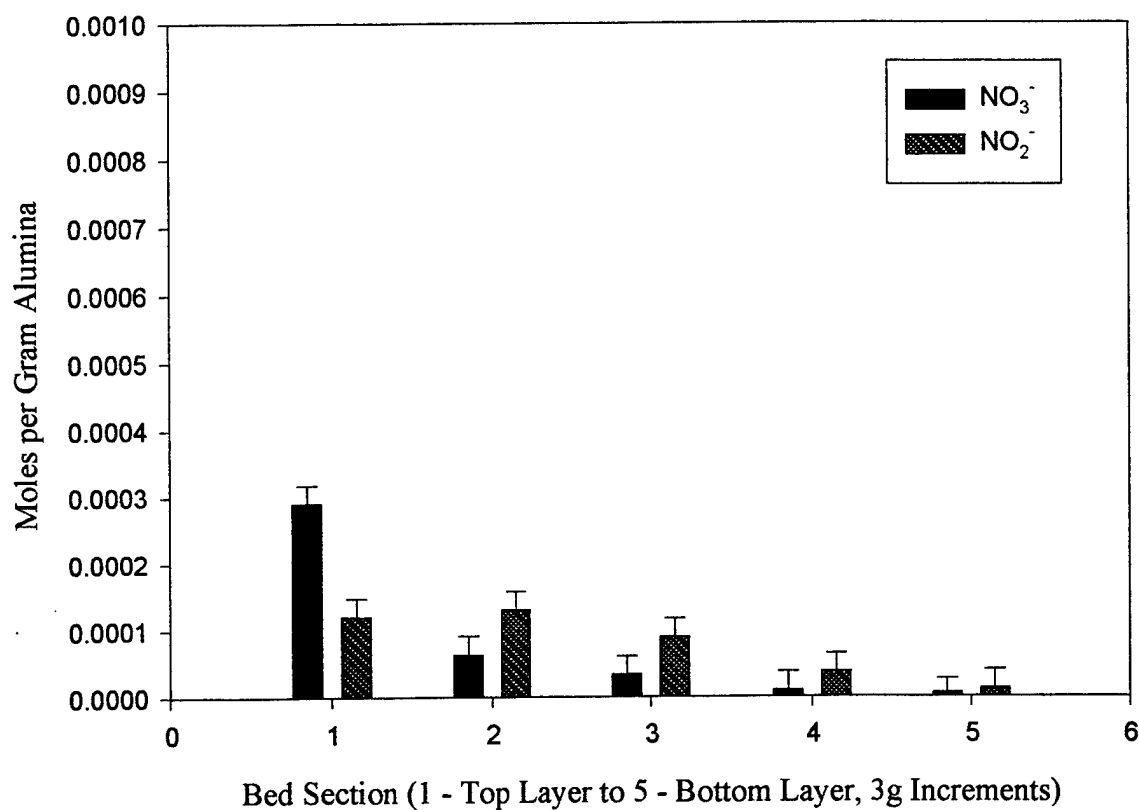
Figure 3-16. Moles Nitrate and Nitrite per Gram Alumina for Sections of the Reactor Bed with K2CO3-Treated Alumina, 30 min Exposure, Error Bars According to 2 Standard Deviations
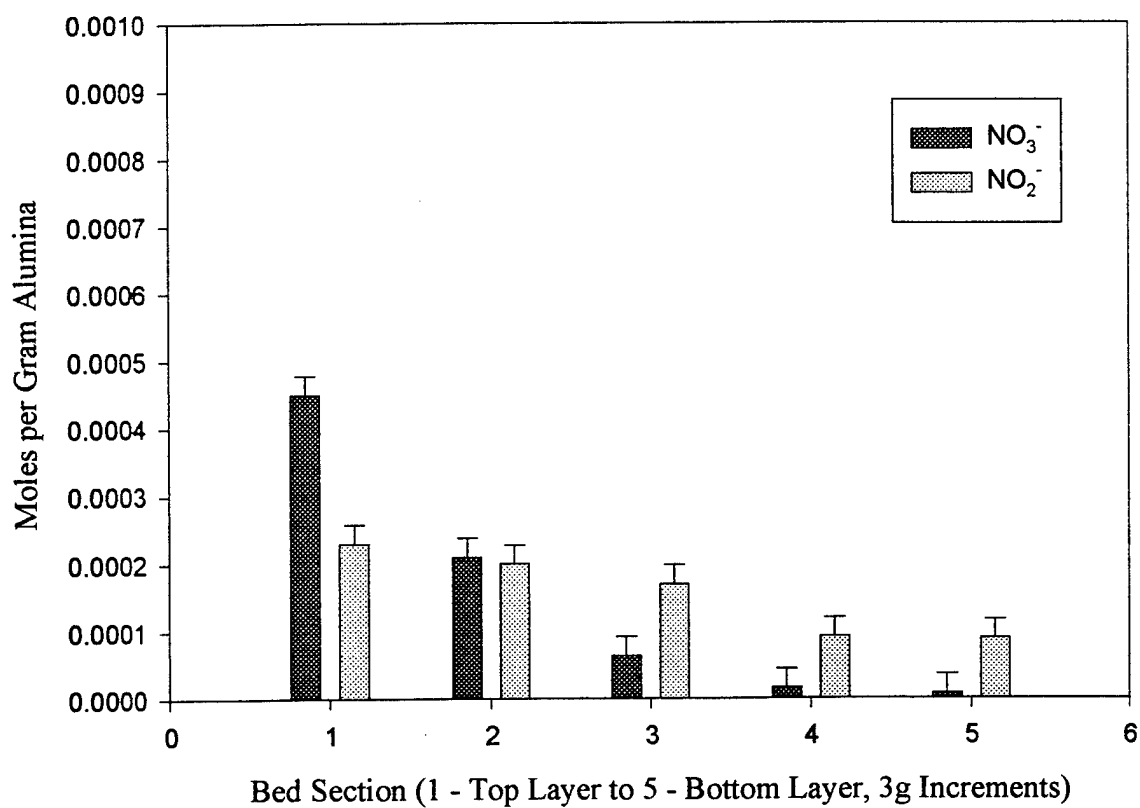
Figure 3-17. Moles Nitrate and Nitrite per Gram Alumina for Sections of the Reactor Bed with K2CO3-Treated Alumina, 60 min Exposure, Error Bars According to 2 Standard Deviations
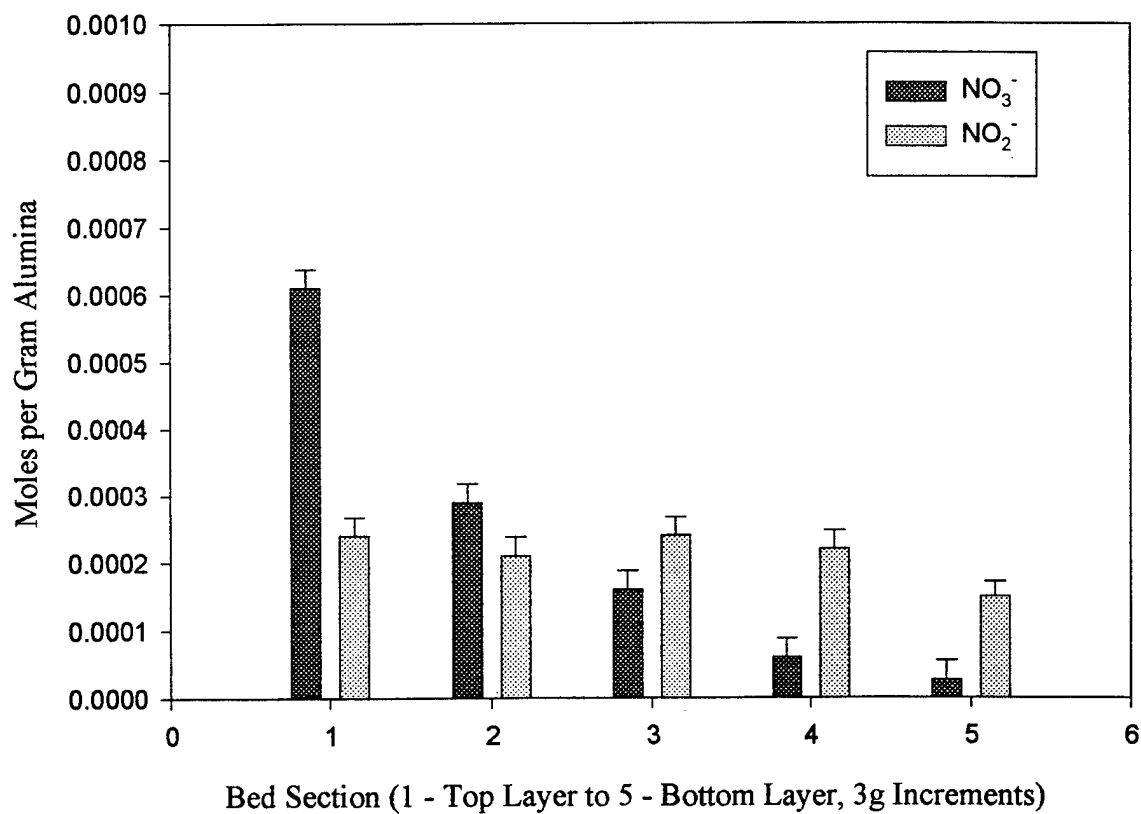
Figure 3-18. Moles Nitrate and Nitrite per Gram Alumina for Sections of the Reactor Bed with K2CO3-Treated Alumina, 90 min Exposure, Error Bars According to 2 Standard Deviations
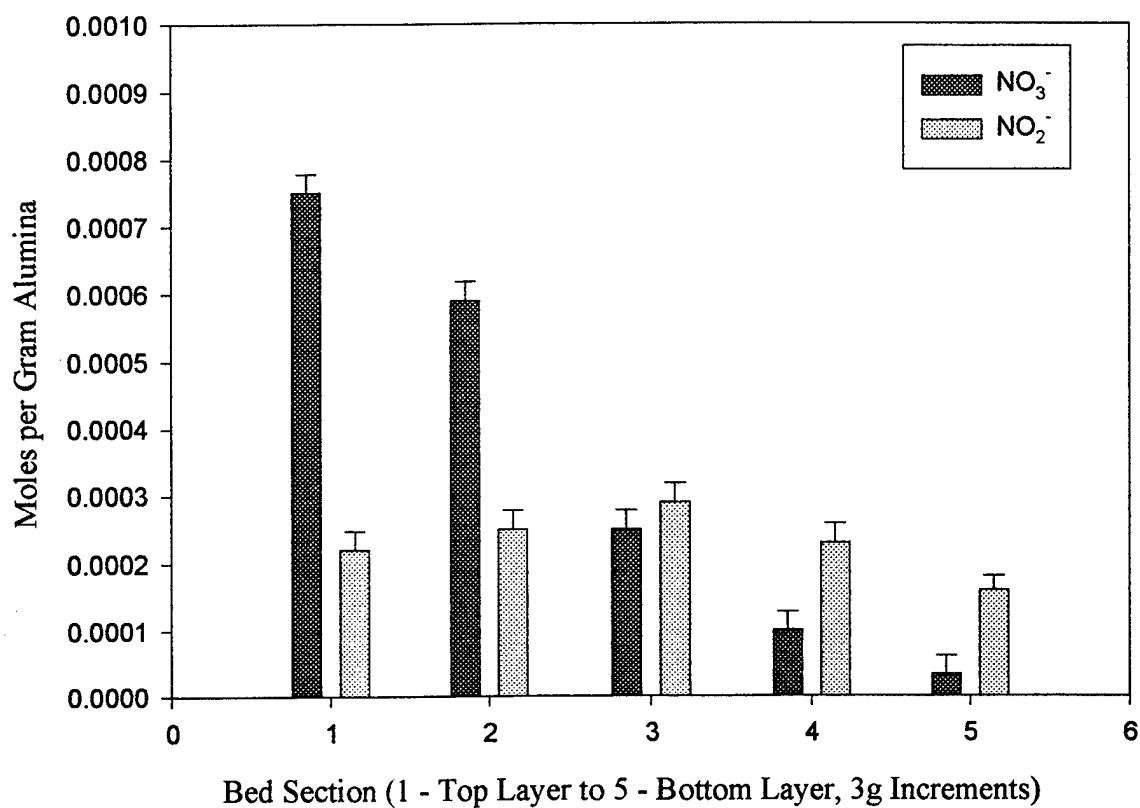
Figure 3-19. Moles Nitrate and Nitrite per Gram Alumina for Sections of the Reactor Bed with K2CO3-Treated Alumina, 120 min Exposure, Error Bars According to 2 Standard Deviations

surface of K_2CO_3-treated alumina than on the untreated alumina for the similar exposures. This is consistent with the findings reported by Lee (1998) and Lee et al. (1998a and 1998b), that alkaline coatings (K_2CO_3 and KOH) enhance NO_x adsorption by alumina. In acidic media nitrite is unstable (particularly at high temperatures) (Choi and Fung, 1980). Nitrite is more stable on the alkaline treated alumina as the high pH of the base acts as a buffer which stabilizes the nitrite as the potassium salt. A relationship between nitrite and pH was observed by Choi and Fung (1980) in their studies of nitrate/nitrite quantification from meat products. They observed the best percent recovery of nitrite when basic solvents were used to extract nitrite from spiked samples. Nitrite recovery of 99% was noted for extraction with borax solvents of pH 9.0 and 10.8. The borax solvent with pH 10.8 was the highest pH tested. While nitrite recovery of 103% was noted for a borax-sulfuric acid solvent of pH 7.8, nitrite recovery decreased from this point to 69% at a pH of 3.1 with a borate-sulfuric acid solvent. Nitrate recovery averaged 100% for all of the pH's tested (Choi and Fung, 1980). As the pH's of the K_2CO_3-treated alumina in this study usually were in the range of 10 to 11, this corresponds to the optimum nitrite recovery range observed by Choi and Fung (1980). It may be presumed that in this optimal pH range, nitrite is more stable, and therefore we may expect nitrite to be more prevalent on K_2CO_3-treated alumina.

KOH-treated alumina

The results from KOH coated alumina are similar to those for K_2CO_3 alumina. The surface NO_x^- measured at the four different exposure times for KOH-treated alumina are shown in Figures 3-20, 3-21, 3-22, and 3-23. As KOH is a stronger base, the buffering
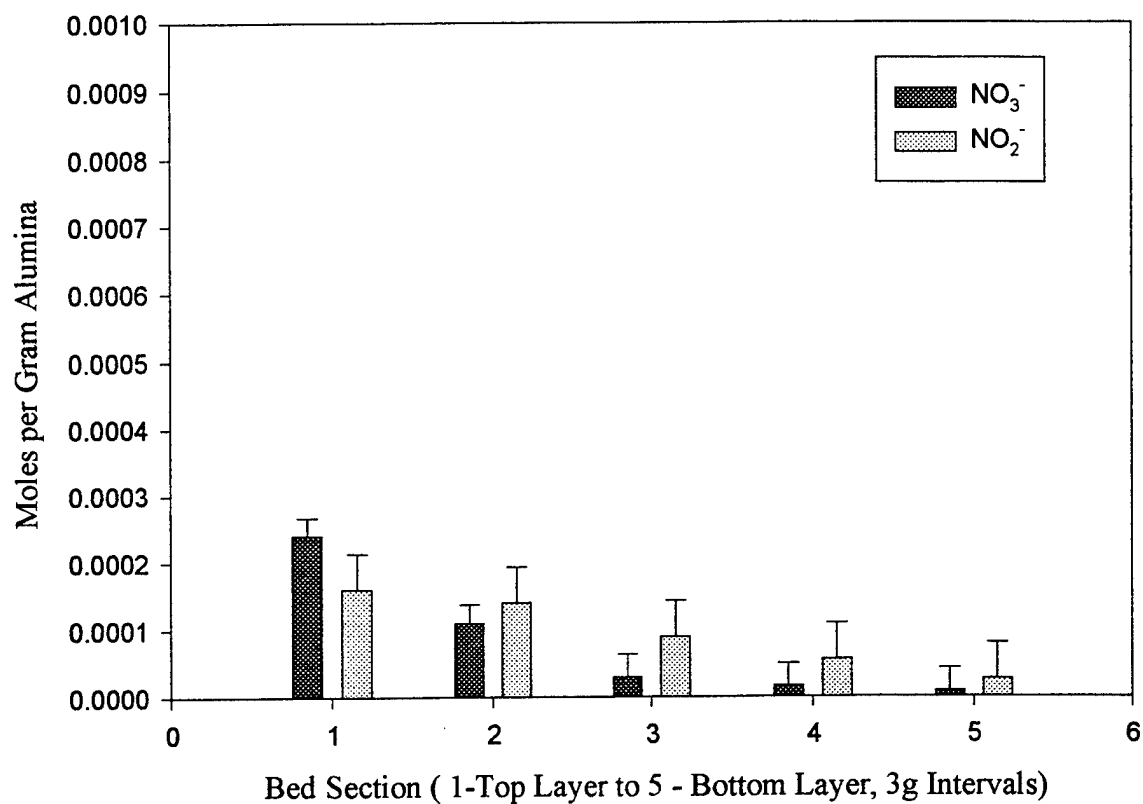
Figure 3-20. Moles Nitrate and Nitrite per Gram Alumina for Sections of the Reactor Bed with KOH-Treated Alumina, 30 min Exposure, Error Bars According to 2 Standard Deviations
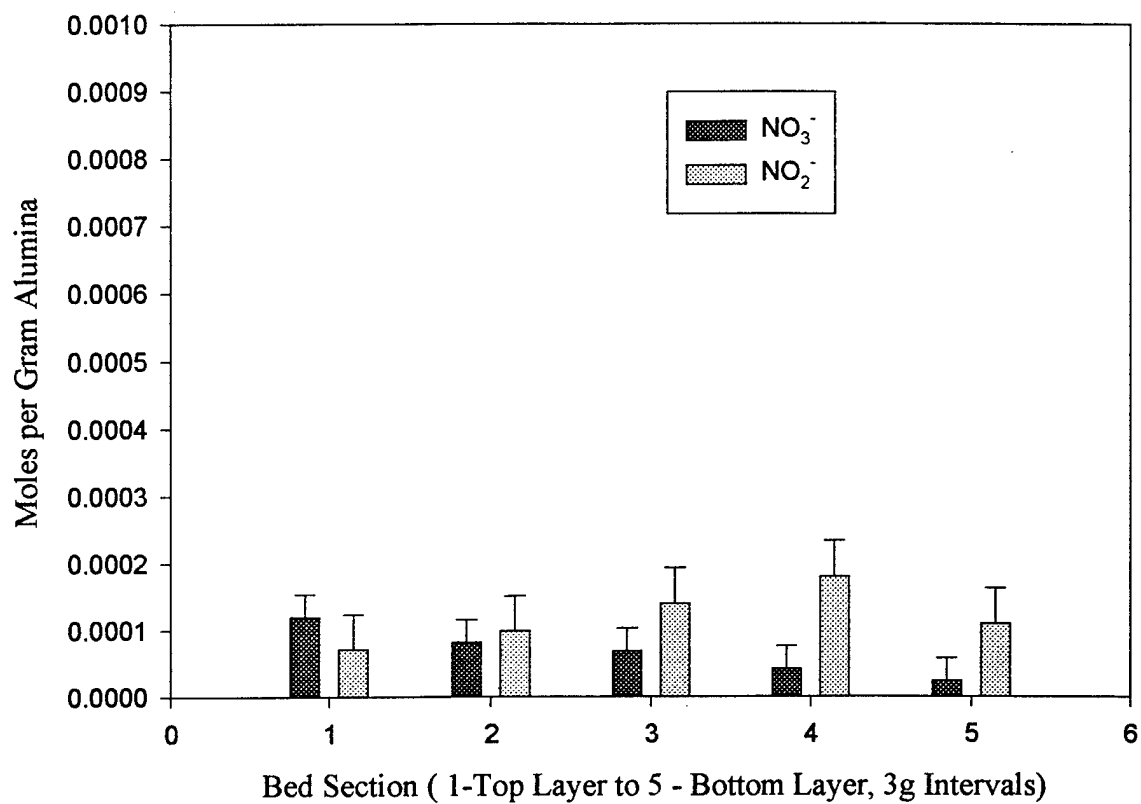
Figure 3-21. Moles Nitrate and Nitrite per Gram Alumina for Sections of the Reactor Bed with KOH-Treated Alumina, 60 min Exposure, Error Bars According to 2 Standard Deviations
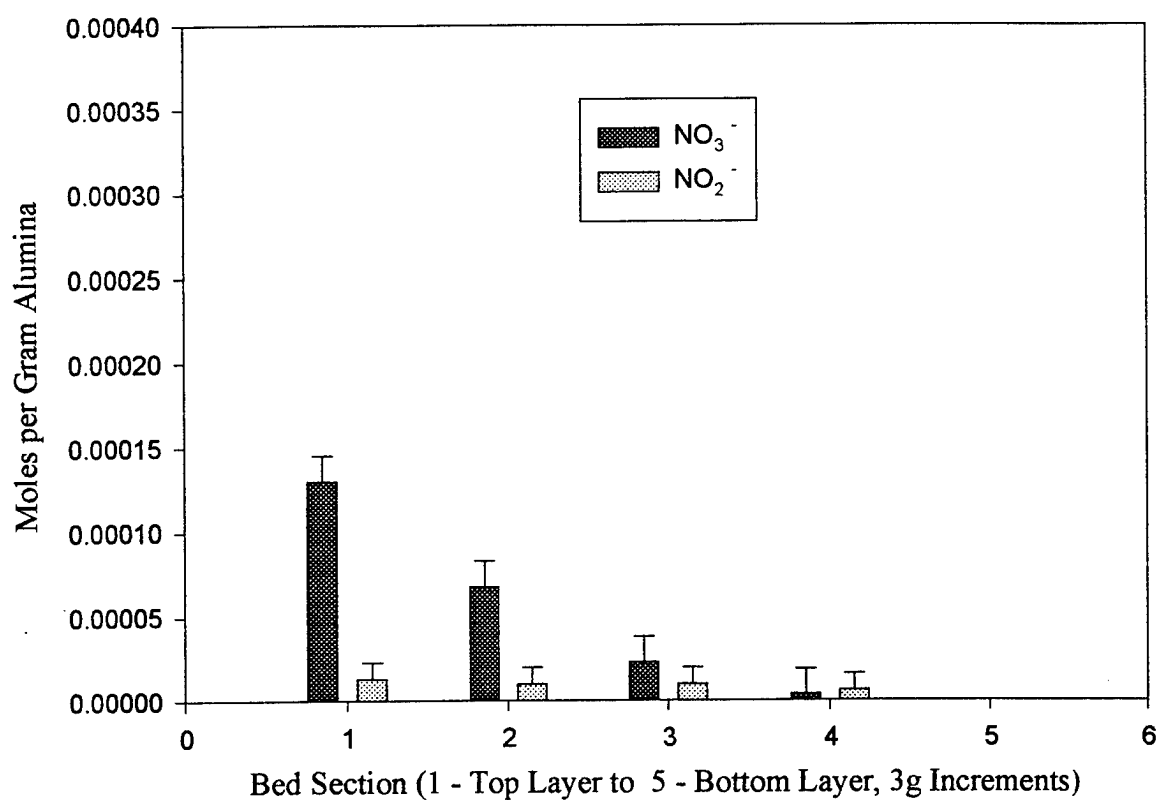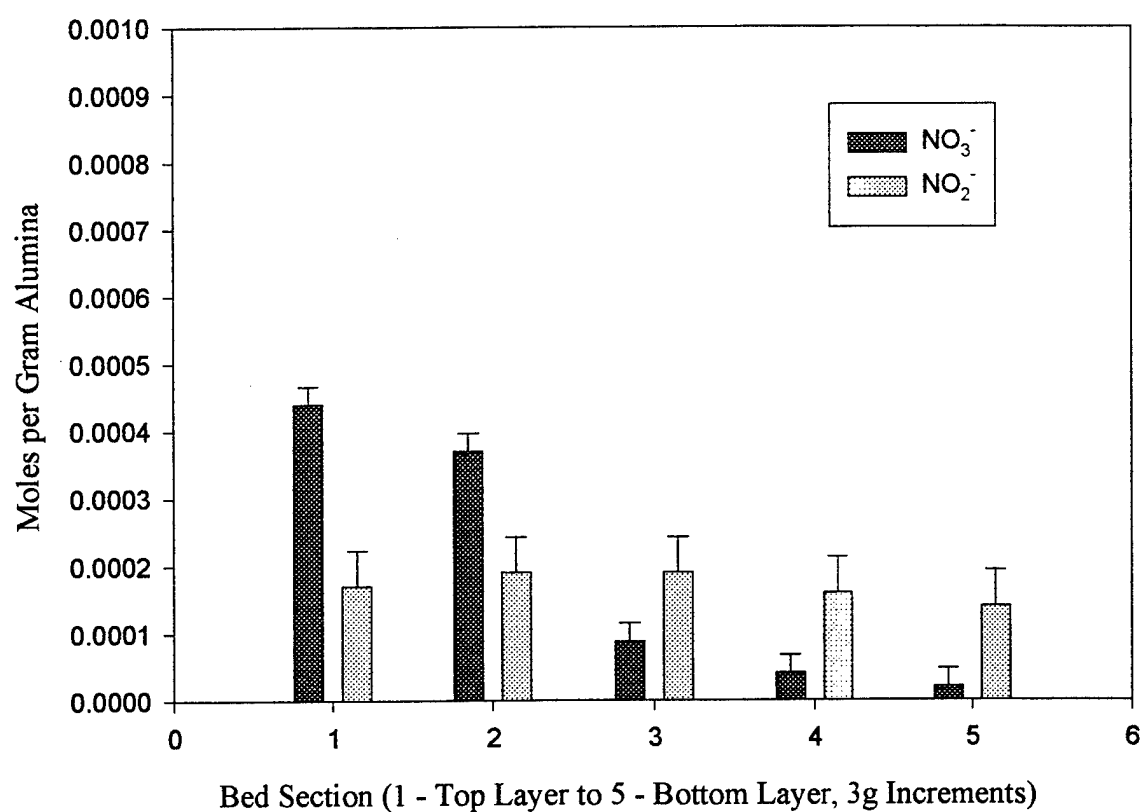
Figure 3-22. Moles Nitrate and Nitrite per Gram Alumina for Sections of the Reactor Bed with KOH-Treated Alumina, 90 min Exposure, Error Bars According to 2 Standard Deviations
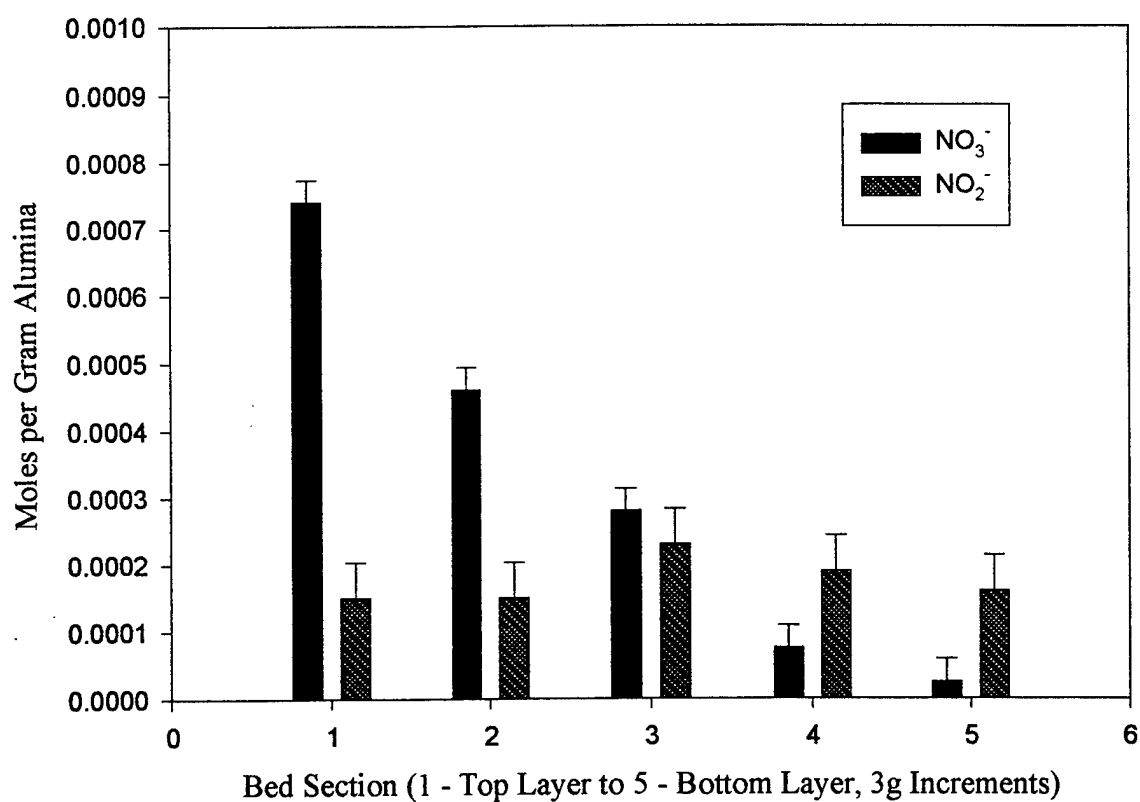
Figure 3-23. Moles Nitrate and Nitrite per Gram Alumina for Sections of the Reactor Bed with KOH-Treated Alumina, 120 min Exposure, Error Bars According to 2 Standard Deviations

action of potassium nitrite is presumably different than for K_2CO_3. No solvents with pH's in the range of those observed for KOH-treated alumina were tested for nitrite/nitrate recovery by Choi and Fung (1980). Note that in Figure 3-21, for the 60 minute exposure, the data does not fit the trends in nitrate and nitrite quantities as in the other exposure times. There was a handling error with this sample. It was possible that the sample was mislabeled. Also, the alumina pellets in the sample may have been mixed so that pellets from different layers were stored in the same vial. As trends in nitrate and nitrite quantities over time are evident from the 30, 90, and 120 minute exposures, the 60 minute data will be excluded from quantitative and qualitative analyses in the following sections.

Quality Control

The Quality Control charts for independent nitrate and nitrite measurements are shown in the Appendix C. The results for the samples with known concentrations are shown as the percent recoveries in concentration determined by the test method. Samples with known NO_x^- concentrations were assayed at the end of a testing day. These samples were made to have similar NO_x^- concentrations of samples which were tested on that specific day. The time period covered is July through October which is when the results related in this study were obtained. From the charts in Appendix C, the error was fairly random and was almost always within the working limits ($\pm 2\sigma$). No values were outside of the control limits ($\pm 3\sigma$). Both nitrate and nitrite measurements, on average, slightly overestimated the independent sample concentrations as shown by the value of the mean which was 105%.

Effectiveness of Alumina Adsorbents

While it is clear that the alkaline treated aluminas are better sorbents for NO_x than untreated alumina, a quantitative measurement of the effectiveness of the sorbent materials may be gained by observing the total moles of NO_x^- present for each material during identical runs. These data are shown in Table 3-4 which lists the sum of the nitrate and nitrite moles present on the surface of the sorbent for each exposure time grouped by alumina treatment. These data, from the longbed series, are the sum of the surface NO_x^- present from the 5 bed layers for each exposure time as shown in previous charts. From Table 3-4, K_2CO_3-treated alumina was the most effective sorbent in this study as more moles of NO_x^- were present on the surface of this alumina type than for the other two. KOH-treated alumina also was an effective NO_x sorbent though not as effective as the K_2CO_3 alumina. KOH-treated alumina initially sorbed a slightly greater amount of moles of NO_x than did K_2CO_3-treated alumina, as reflected in the total NO_x^- present after 30 minutes, but the latter sorbed more moles of NO_x over the duration of the total run. Through observation of the total moles sorbed for all the exposure times, the alkaline-treated aluminas were at least twice as effective as NO_x adsorbers than untreated alumina.

The weight percents of the treatment compounds with respect to the sorbent weight were 25% and 20% for KOH and K_2CO_3-treated alumina, respectively. These weight percents were found by Lee et al. (1998a) to correspond to the optimum sorption of NO_x.

Table 3-4. Total Moles of NO_x^- Present on the Sorbent Surface for Each Exposure Time and Treatment Type

Exposure (min)	Untreated	K2CO3	KOH
30	2.6E-04	7.8E-04	8.8E-04
60	4.8E-04	1.5E-03	9.3E-04*
90	8.2E-04	2.2E-03	1.8E-03
120	1.1E-03	2.9E-03	2.5E-03

* Indicates invalid data

Sorption and Production of NO

A characteristic of NO_x adsorption by untreated and treated alumina is that NO gas is produced during the adsorption process. This NO production has been noted by other researchers (Kimm et al., 1995; Nelli and Rochelle, 1996; Lee, 1998; and Lee et al., 1998a and 1998b) as described earlier. While NO is produced almost immediately when untreated alumina is the sorbent, NO production is delayed when the alumina is treated with the alkaline compounds considered in this investigation (Lee et al., 1998a and 1998b). This delay may be due to the nature of the compounds formed at the alumina surface during NO_x adsorption. This possibility will be discussed later.

None of the treated aluminas in this study adsorbed NO when NO was the only constituent of the airstream. However, when the airstream consists of both NO and NO_2, NO is initially sorbed by the alkaline-treated aluminas, though after a certain time exposure, NO is produced in the process. Studies by Lee (1998) and Lee et al. (1998a) found that in order for NO to be sorbed (on the alkaline-treated aluminas), NO_2 must also be present. This situation indicates that a simultaneous reaction between NO, NO_2, and the treatment material may play a role in the adsorption mechanism. NO sorption on untreated alumina was negligible except for the case when the airstream concentration of NO was similar to that of NO_2. Sorption of NO for this case was minimal but was nonetheless significant, though to a much less degree than was observed for the treated aluminas.

Coordination of Surface and Gaseous NO$_x$ Data

Comparisons of the nitrate and nitrite quantities present on the surface of the alumina sorbents with the associated gaseous NO$_x$ sorbed in the bed are useful in determining material balances and confirming possible mechanisms of the sorption processes. Max Lee provided the gaseous data from the reactor bed exposures.

Airstream NO$_x$ Concentrations

Fixed bed runs were performed by Max Lee in which the ratio of NO$_2$:NO in the airstream was varied. The concentration of NO$_2$ was held at 500 ppm while the concentration of NO was varied. Nitrate and nitrite quantities were measured on the sorbent surfaces for these runs. These data are presented in Figures 3-24, 3-25, and 3-26 for the three sorbents at a temperature of 200C. Note the vertical scale in these figures is in units of moles per gram alumina per minute, which represents the rate of formation of the nitrate/nitrite species on the sorbent. These units are used as the run times for the bed exposures varied from 130 to 180 minutes. In Figure 3-24, for untreated alumina, the rate of formation of nitrate varies within experimental errors as the NO concentration increases. There is minimal nitrite formation for all the cases. In Figures 3-25 and 3-26 for the treated aluminas, the formation of nitrite increases as [NO] increases. In Figure 3-25 for K$_2$CO$_3$-treated alumina, there is an associated decrease in nitrate formation as [NO] increases in the airstream. This decrease in nitrate with increasing [NO] is still evident, though to a lesser degree for KOH-treated alumina in Figure 3-26. Through Figures 3-25 and 3-26, nitrite formation is heavily favored over that of nitrate for the latter case where [NO] and [NO$_2$] in the feed gas are both 500 ppm. This observation indicates that an
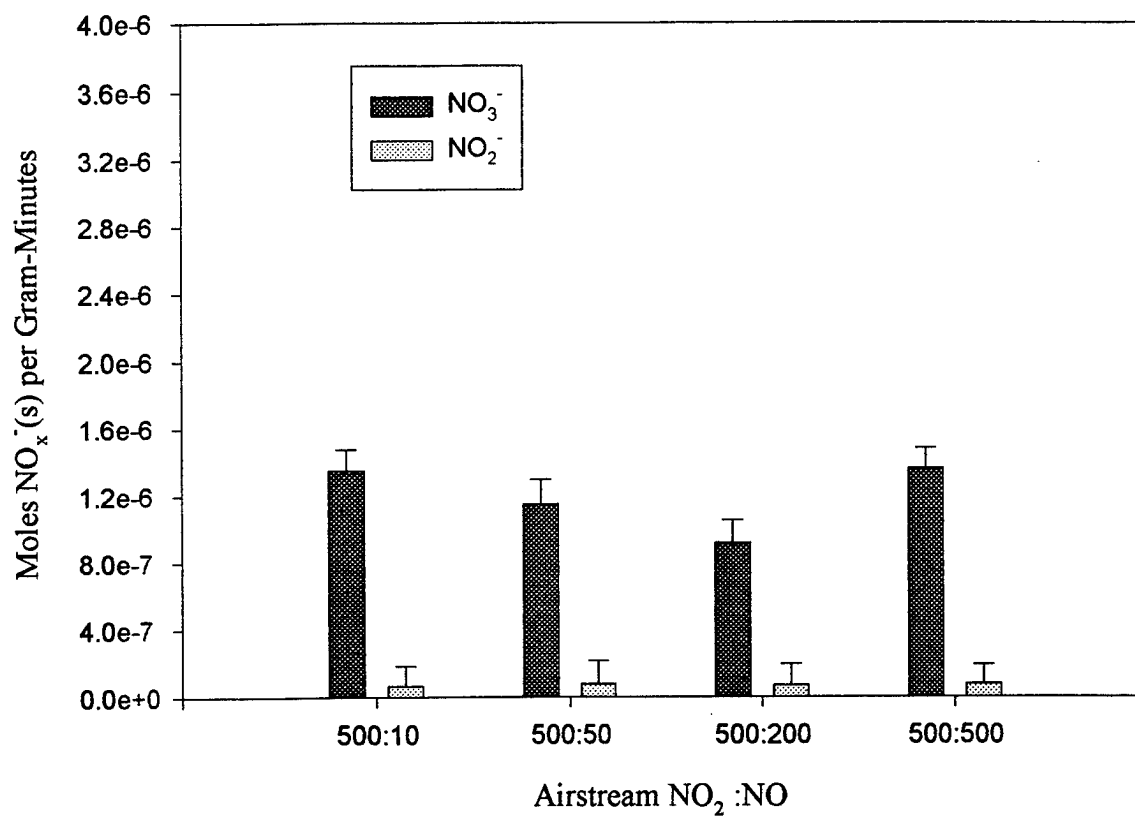
Figure 3-24. Nitrate and Nitrite Moles per Gram Alumina per Minute Exposure Time for Untreated Alumina Exposed to Varying NO Concentrations in Airstream, 200C
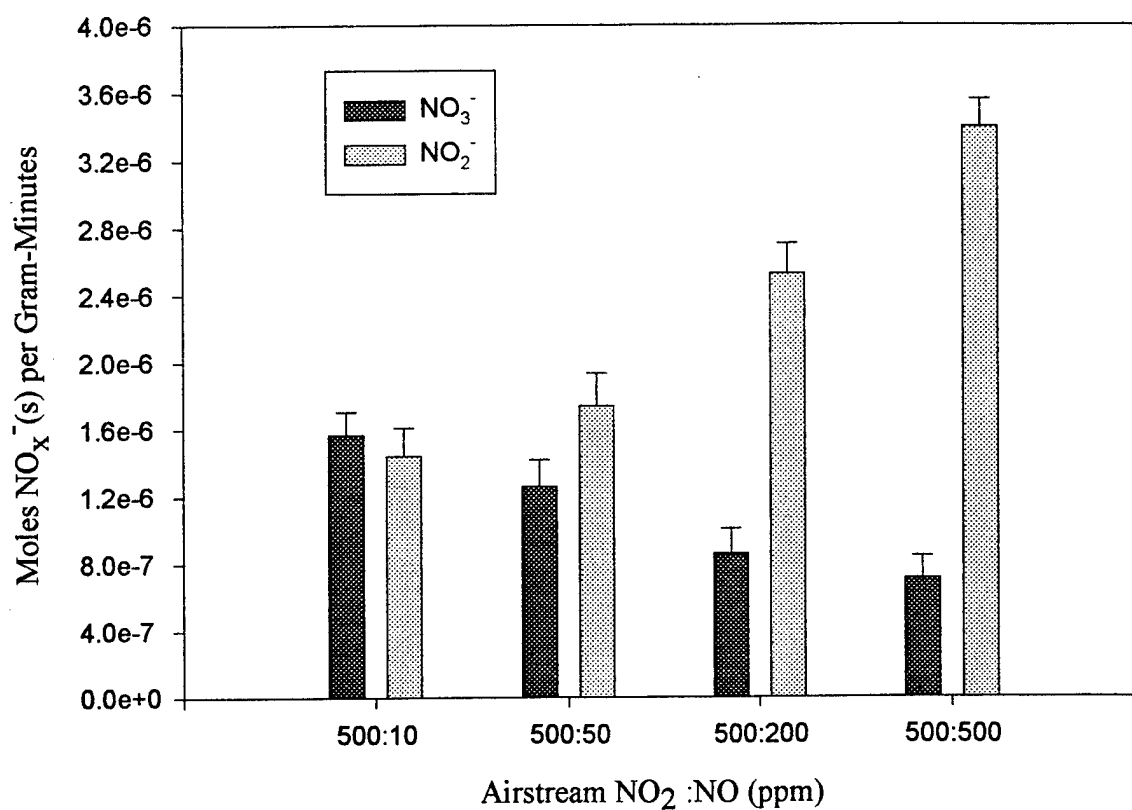
Figure 3-25. Nitrate and Nitrite Moles per Gram Alumina per Minute Exposure Time for K2CO3-Treated Alumina Exposed to Varying NO Concentrations in Airstream, 200C

A: 128 min exposure
B: 158 min exposure
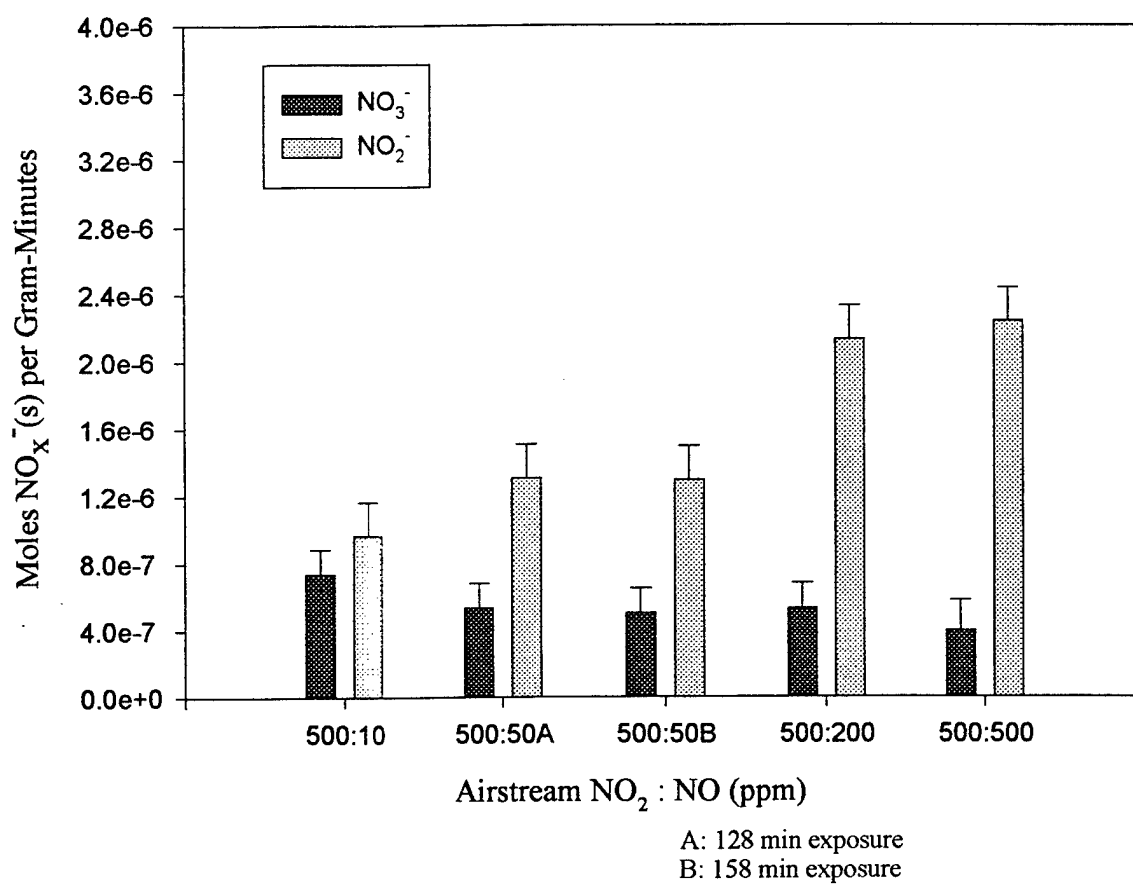
Figure 3-26. Nitrate and Nitrite Moles per Gram Alumina per Minute Exposure Time for KOH-Treated Alumina Exposed to Varying NO Concentrations in Airstream, 200C

increased amount of NO in an airstream favors nitrite formation on alkaline-treated

alumina. However, as pointed out in the previous section, the presence of NO_2 is required

for this sorption of NO to occur. It is likely that NO, NO_2, and the treatment material

undergo a simultaneous reaction and, that without NO_2, this reaction cannot transpire.

Longbed Series NO_x Uptake and Surface NO_x^-

Using the nitrate/nitrite data from the longbed runs discussed in the last section,

key trends may be observed when comparing ratios of these species with each other and

with the amounts of NO_2 sorbed and/or the amounts of NO produced. The gaseous NO_x

data were obtained from Max Lee and manipulated to permit quantitative comparisons

with surface nitrate/nitrite quantities, as determined in the previous section. NO_x

concentrations at the reactor bed outlet were monitored over time for the longbed runs

discussed in the last section. In order to facilitate the analyses on a per-layer basis, Lee

reproduced the longbed runs using 3, 6, 9, 12, and 15g alumina beds and monitored the

outlet concentrations of both NO and NO_2. Essentially, these runs allowed for layer-

specific analyses as cumulative nitrate, nitrite, and NO_x gas sorbed could be analyzed for

each layer. The gaseous uptake data are displayed in Table 3-5. In Table 3-5, analyses

are considered on a layer-specific basis from the longbeds. For each layer, data are

grouped according to treatment and exposure time. The measured quantities which are

listed in Table 3-5 include the cumulative moles of NO and NO_2 sorbed per gram and per

layer. Differential NO and NO_2 moles, which are the moles of these species sorbed on

each layer, were found by taking the number of total moles sorbed for a layer and

subtracting the total moles sorbed from the previous layer. Nitrate and nitrite quantities

Table 3-5. NOx Sorbed and Nitrate and Nitrite Formed from the Untreated Longbed

3g Exp. Time	UN NO umol/g	NO2 umol/g	total umole NO	total umole NO2	NO+NO2	difference of layers NO	difference of layers NO2	NO2/NO	total umoles NO3-	total umoles NO2-	ratio total NOx-/total NOx
30	-120	345	-360	1035	675	-360	1035	-2.88	390	39	0.636
60	-180	516	-540	1548	1008	-540	1548	-2.87	660	66	0.720
90	-226	645	-678	1935	1257	-678	1935	-2.85	960	26.1	0.784
120	-256	740	-768	2220	1452	-768	2220	-2.89	1110	0	0.764

6g Exp. Time	UN NO umol/g	NO2 umol/g	total umole NO	total umole NO2	NO+NO2	difference of layers NO	difference of layers NO2	NO2/NO	total umoles NO3-	total umoles NO2-	ratio total NOx-/total NOx
30	-97	288	-582	1728	1146	-222	693	-2.97	594	69	0.579
60	-160	460	-960	2760	1800	-420	1212	-2.88	1050	111	0.645
90	-209	594	-1254	3564	2310	-576	1629	-2.84	1680	59.1	0.753
120	-245	695	-1470	4170	2700	-702	1950	-2.84	1980	33	0.746

9g Exp. Time	UN NO umol/g	NO2 umol/g	total umole NO	total umole NO2	NO+NO2	difference of layers NO	difference of layers NO2	NO2/NO	total umoles NO3-	total umoles NO2-	ratio total NOx-/total NOx
30	-72	230	-648	2070	1422	-66	342	-3.19	663	99	0.536
60	-136	416	-1224	3744	2520	-264	984	-3.06	1191	150	0.532
90	-192	572	-1728	5148	3420	-474	1584	-2.98	2070	104.1	0.636
120	-236	692	-2124	6228	4104	-654	2058	-2.93	2640	72	0.661

12g Exp. Time	UN NO umol/g	NO2 umol/g	total umole NO	total umole NO2	NO+NO2	difference of layers NO	difference of layers NO2	NO2/NO	total umoles NO3-	total umoles NO2-	ratio total NOx-/total NOx
30	-51	181	-612	2172	1560	36	102	-3.55	674.1	117	0.507
60	-106	340	-1272	4080	2808	-48	336	-3.21	1233	186	0.505
90	-161	495	-1932	5940	4008	-204	792	-3.07	2202	131.4	0.582
120	-209	624	-2508	7488	4980	-384	1260	-2.99	2970	114	0.619

15g Exp. Time	UN NO umol/g	NO2 umol/g	total umole NO	total umole NO2	NO+NO2	difference of layers NO	difference of layers NO2	NO2/NO	total umoles NO3-	total umoles NO2-	ratio total NOx-/total NOx
30	-39	148	-585	2220	1635	27	48	-3.79	674.1	117	0.484
60	-81	280	-1215	4200	2985	57	120	-3.46	1240.2	205.5	0.484
90	-127	418	-1905	6270	4365	27	330	-3.29	2301	156.6	0.563
120	-172	546	-2580	8190	5610	-72	702	-3.17	3111	147	0.581
										AVG	0.62
										SD	0.10

were determined for each layer by using the mole per gram amounts determined above and using calculations similar to those in Table 3-5 for the gaseous data. In Table 3-5, only the gaseous data from the runs with untreated alumina have been included as the data are rather voluminous. The rest of the data, including the NO_x uptake for the treated materials, the nitrate/nitrite quantities, and indicative molar ratios can be found in Appendix D.

NO$_x$ Percent Recovery: Longbed Series

In order to ascertain the reliability of the data obtained from the longbed series, surface NO_x^- quantities were correlated to gaseous input and output quantities of NO_x observed for the longbed series exposures. When the total number of moles of output NO_x gas measured in the reactor bed are subtracted from the total moles of NO_x gas input into the reactor bed, the remaining amount should equal the molar sum of the nitrate and nitrite which is formed on the alumina surface if all reactants and products are identified and measured in material balances:

$$NO_{x(g)IN} - NO_{x(g)OUT} = NO_{x\ (s)SURFACE}^-$$
(3-1)

Using the data from Table 3-5 (and Appendix D), molar sums of nitrate, nitrite and NO_x sorbed can be determined for each bed layer. From these analyses, the percent recovery of the ISE method can be tested by calculating the ratio of NO_x^- to NO_x sorbed for each layer. This data is shown in Table 3-6. From Table 3-6, the total percent recoveries for the various sorbents were 62%, 122%, and 100%, for untreated, K_2CO_3, and KOH, respectively. The percent recoveries were higher for layer 1 of the longbed and decreased by layer. Layer 1 had the greatest amount of nitrate and nitrite as it was the most exposed

Table 3-6. Percent Recovery, NO_x^-/NO_x Sorbed, for Longbed Series

Layer	Untreated	K2CO3	KOH
1	73	135	105
2	68	130	100
3	59	117	98
4	55	114	95
5	53	116	99
Bed Average	62	122	100
SD (σ)	10	11	3.6

layer. and layer 5 had the least amount of these species as it was the least exposed.

Nitrate and nitrite on K_2CO_3-treated alumina were overestimated by 22% for the total

longbed. KOH percent recovery was 100% for the total longbed.

Due to the low and high recoveries for the untreated and K_2CO_3-treated samples,

respectively, and the invalid data acquired from the 60 minute exposure for the KOH-

treated samples, further tests were performed to confirm that the trends in NO_x sorption

and the corresponding NO_x^- formation observed in the longbed series were real. Also,

there was concern over the per-layer NO_x uptakes as this gaseous data was acquired from

reproduced runs (which were not tested for NO_x^-). Degradation of NO_x^-, particularly for

untreated alumina, was also likely as a source of the low recoveries for these samples as it

was later determined that the best percent recoveries (NO_x sorbed / NO_x^- formed) for all

the sorbents were achieved when the testing for nitrate and nitrite was performed

immediately after the sorbents were exposed to NO_x in the fixed bed. The degradation of

surface NO_x^- was found to be significant on a daily rather than on a monthly basis. This

degradation of NO_x^- on the untreated alumina was observed to be as much as 25% after

one day of storage. As the untreated samples from the longbed series were tested for

NO_x^- one day after they were exposed to NO_x, significant degradation may have occurred

during this one-day storage and this may explain the rather low recoveries observed for

the untreated longbed samples.

Total System Error and Percent Recovery

Alumina samples which are tested for nitrate and nitrite immediately after exposure

in the fixed bed showed the best percent recoveries as mentioned above. Several of these

samples were used to confirm trends observed in the longbed studies and also to determine the degree of error which was inherent in the overall exposure-testing systems used conjunctively by Max Lee and the author of this thesis. The results from this percent recovery / error analysis are shown in Table 3-7. The samples in Table 3-7 are from three 'identical' exposures to NO_x. There is some variation in these exposures from the fixed bed system used by Max Lee which are related through the calculations of the mean, standard deviation, 95% confidence interval (CI), and the 95% CI fraction which is the 95% CI divided by the mean. This variation is fairly low as the 95% CI is about 7%-8% of the mean (95% CI fraction) for untreated and treated aluminas.

Measurement of nitrate and nitrite on these samples also showed variation on the order of 7% for untreated and KOH-treated alumina. The 95% CI fraction for K_2CO_3-treated alumina was 14%, indicating that variation in the measurement of nitrate and nitrite on these samples was twice as much as that for the other two sample types.

Overall accuracy (recovery) of the testing systems used in these investigations can be determined through comparison of the molar sums of the total NO_x sorbed and the total NO_x^- species measured on the sorbents. In Table 3-7 the percent recoveries (NO_x sorbed / NO_x^- formed) and standard deviations in these recoveries from the three tests were 86 ±3% for the untreated samples; 112 ±3% for the KOH-treated samples; and 123 ±6% for the K_2CO_3-treated samples. The low and high recoveries for the untreated and treated samples, respectively, is likely due to the nitrate and nitrite testing methods which tend to underestimate and overestimate NO_x^- quantities on these respective sample types. Ionic strength considerations may be a factor here, particularly with the K_2CO_3-treated samples

Table 3-7. Percent Recoveries and Analytical Systems Error for Alumina Samples Tested for NO3- and NO2- Immediately After Exposure to NOx

NOx and NOx- Units are umoles/g

Untreated	NO Sorbed	NO2 Sorbed	NOx Sorbed	NO2- Measured	NO3- Measured	Surface NOx-	Recovery NOx- / NOx
Test 1	-116.7	332.7	216.0	9.2	175	184.2	0.85
Test 2	-112.8	329.5	216.7	8.6	187	195.6	0.90
Test 3	-114.9	342.9	228.0	8.8	182	190.8	0.84
Mean	-114.8	335.0	220.2	8.9	181	190.2	0.86
SD	2.0	7.0	6.7	0.3	6.0	5.7	0.03
95% CI	4.4	15.8	16.5	0.7	13.5	13.5	8.22
95% CI / Mean			0.07				0.09

NOx and NOx- Units are umoles/g

K2CO3	NO Sorbed	NO2 Sorbed	NOx Sorbed	NO2- Measured	NO3- Measured	Surface NOx-	Recovery NOx- / NOx
Test 1	-28.9	280.7	251.8	146	168	314	1.25
Test 2	-32.3	298.5	266.2	144	198	342	1.28
Test 3	-28.1	288.3	260.2	140	162	302	1.16
Mean	-29.8	289.2	259.4	143	176	319	1.23
SD	2.2	8.9	7.2	3.1	19.3	20.5	0.06
95% CI	5.1	20.2	20.8	6.9	43.7	44.2	0.14
95% CI / Mean			0.08				0.12

NOx and NOx- Units are umoles/g

KOH	NO Sorbed	NO2 Sorbed	NOx Sorbed	NO2- Measured	NO3- Measured	Surface NOx-	Recovery NOx- / NOx
Test 1	-25.6	276.5	251.0	144	138	282	1.12
Test 2	-25.7	282.4	256.8	153	144	297	1.16
Test 3	-26.3	293.4	267.1	141	150	291	1.09
Mean	-25.8	284.1	258.3	146.0	144	290	1.12
SD	0.4	8.6	8.2	6.2	6.0	7.5	0.03
95% CI	0.9	15.8	19.4	0.7	13.5	19.6	0.08
95% CI / Mean			0.08				0.07

as the valence of the carbonate ion, -2, affects the ionic strength of these solutions by a power of two. For the testing of NO_x^- concentrations from the K_2CO_3-treated samples, small variations in the concentration of carbonate ion in the standard and sample solutions can cause the ionic strengths of the sample and standard solutions to also vary, and hence, error in concentration measurements may occur. Equalization of ionic strength was attempted through the equalization of the pH of standard and sample solutions. It was not uncommon for the pH of standard and sample solutions to vary slightly (from $\pm$ .1-.2 pH units), which would affect the respective ionic strengths. Note that for the KOH-treated samples, percent recoveries were closer to 100%. This may indicate that, as hydroxide ion has a valence of -1, a small variation in hydroxide ion concentration has less of an effect on the ionic strength of a solution than does the same variation of carbonate ion. In this way, exact equalization of pH between sample and standard solutions is likely more crucial in the NO_x^- testing of K_2CO_3-treated alumina samples as small variations in carbonate ion (pH) may significantly affect ionic strength.

<u>Proposed Mechanisms</u>

According to the gaseous and surface NO_x results from the longbed series, the varied NO series, and all other pertinent knowledge of NO_x interactions with the alumina and treatment compounds used in this study, the following mechanisms of interaction of NOx with untreated and treated aluminas are being proposed to explain the detailed and extensive investigation of Lee (1998). Though the longbed recoveries were not the optimal 100%, these data are included as important trends can be observed as exposure time (to NO_x) increases.

Untreated Alumina

$$Al_2O_{3(s)} + 6NO_{2(g)} \rightarrow Al(NO_2)_{3(s)} + Al(NO_3)_{3(s)} \qquad (3\text{-}2)$$

$$2Al(NO_2)_{3(s)} \rightarrow Al_2O_{3(s)} + 3NO_{2(g)} + 3NO_{(g)} \qquad (3\text{-}3)$$

$$Al(NO_2)_{3(s)} + 3NO_{2(g)} \rightarrow Al(NO_3)_{3(s)} + 3NO_{(g)} \qquad (3\text{-}4)$$

Overall: $\qquad Al_2O_{3(s)} + 9NO_{2(g)} \rightarrow 2Al(NO_3)_{3(s)} + 3NO_{(g)} \qquad (3\text{-}5)$
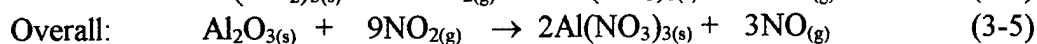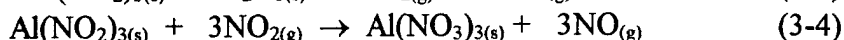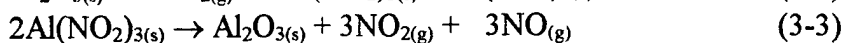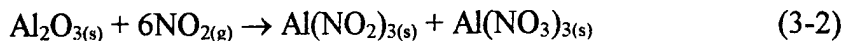
Initially, NO_2 is sorbed on alumina in (3-2) to form aluminum nitrate and nitrite species. The aluminum nitrite species which is formed in (3-2) may either decompose (3-3) or react with NO_2 gas (3-4). The reactions in (3-3) and (3-4) are presumably rapid due to the instability of the aluminum nitrite species. Over time, nitrate species should heavily outweigh nitrite species as the nitrite would have reacted or decomposed. On tested samples, only trace amounts of nitrite were present.

Cumulative uptake of NO_2 and NO is plotted along with the cumulative formation of nitrate and nitrite for layer 1 of the untreated alumina longbed in Figure 3-27. In (3-5), a 3 to 1 ratio of NO_2 sorbed to NO produced is proposed. In Figure 3-27, it is seen that this ratio appears to converge towards 3 over time.

According to the overall reaction (3-5), there should be a 3:2 ratio of NO_2 sorbed to nitrate produced. In Figure 3-2, this appears to be the case as exposure time increases. Note that since there was only 73% recovery from the untreated layer 1, the nitrate quantities are slightly underestimated.

K$_2$CO$_3$-Treated Alumina

In the early stages of NOx sorption by K_2CO_3-treated alumina, both NO_2 and NO are sorbed. The following mechanisms have been proposed with this in mind:
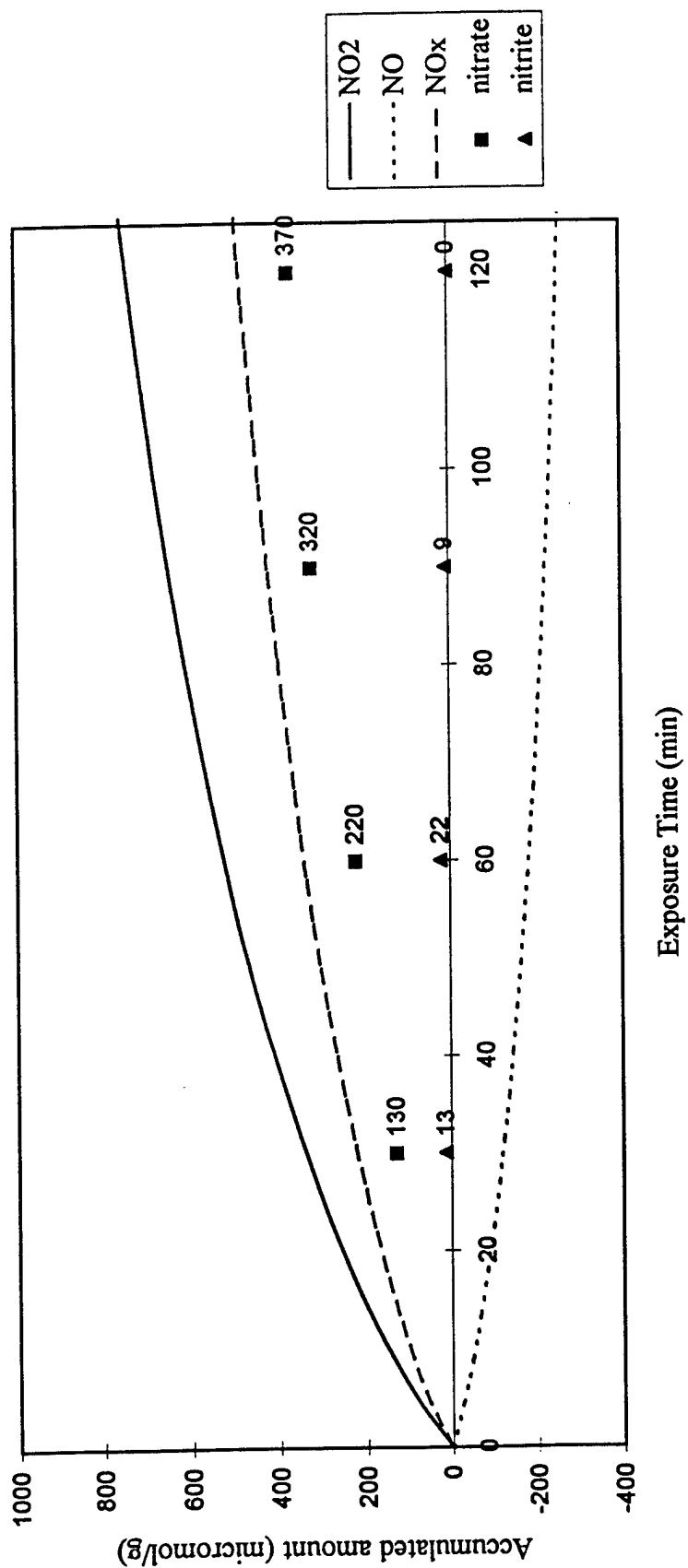
Figure 3-27. Cumulative NO2 and NO Uptake and Nitrate and Nitrite Formation from Untreated Longbed, Layer 1, 25C

$$K_2CO_{3(s)} + 2NO_{2(g)} \rightarrow KNO_{2(s)} + KNO_{3(s)} + CO_{2(g)} \qquad (3\text{-}6)$$

$$K_2CO_{3(s)} + NO_{(g)} + NO_{2(g)} \rightarrow 2KNO_{2(s)} + CO_{2(g)} \qquad (3\text{-}7)$$

Overall: $\quad 2K_2CO_{3(s)} + 3NO_{2(g)} + NO_{(g)} \rightarrow KNO_{3(s)} + 3KNO_{2(s)} + 2CO_{2(g)} \qquad (3\text{-}8)$
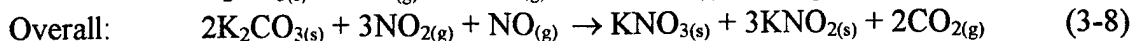
Equation (3-7) is included as NO is initially sorbed on the treated materials when NO_2 is

also present . The mechanism proposed here is pertinent for low exposure times when NO

is sorbed. Initially, according to (3-8), there should be three times as much nitrite as

nitrate formed on the sorbent surface depending on the availability of NO and NO_2. From

the longbed run at 30 minutes exposure, the average NO_2/NO_3^- from the bottom 3 layers

(least exposed) does in fact equal 3. This ratio for the first two layers of the 30 minute

exposure has already decreased below 3 as the mechanism outlined above is no longer

dominant. As exposure to NO_x increases, nitrate forms from the reaction of NO_2 with the

$KNO_{2(s)}$ formed in (3-6) and (3-7), and NO is produced. The reaction in (3-6) can also

proceed as for initial exposures:

$$K_2CO_{3(s)} + 2NO_{2(g)} \rightarrow KNO_{2(s)} + KNO_{3(s)} + CO_{2(g)} \qquad (3\text{-}6)$$

$$KNO_{2(s)} + NO_{2(g)} \rightarrow KNO_{3(s)} + NO \qquad (3\text{-}9)$$

Overall: $\quad K_2CO_{3(s)} + 3NO_{2(g)} \rightarrow 2KNO_{3(s)} + CO_{2(g)} + NO_{(g)} \qquad (3\text{-}10)$
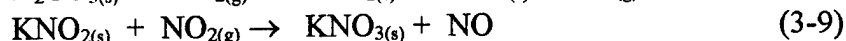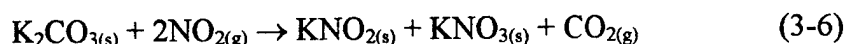
The potassium nitrite formed on the alkaline-treated sorbent is presumably more stable and

less reactive with NO_2 than aluminum nitrite presumably formed on untreated alumina.

Thus, NO production (3-9) is delayed. As NO_x sorption progresses, nitrate builds up and

NO is produced. Reaction (3-9) occurs after reactions (3-6) and (3-7). Note that though

NO is not sorbed unless NO_2 is present, conversely, sorption of NO_2 does not require the

presence of NO, and hence, (3-5) must be included. The cumulative uptake of NO_2 and

NO with the corresponding formation of nitrate and nitrite is shown in Figure 3-28. In

Figure 3-28, the nitrate and nitrite values are overestimated by 35% on average as shown
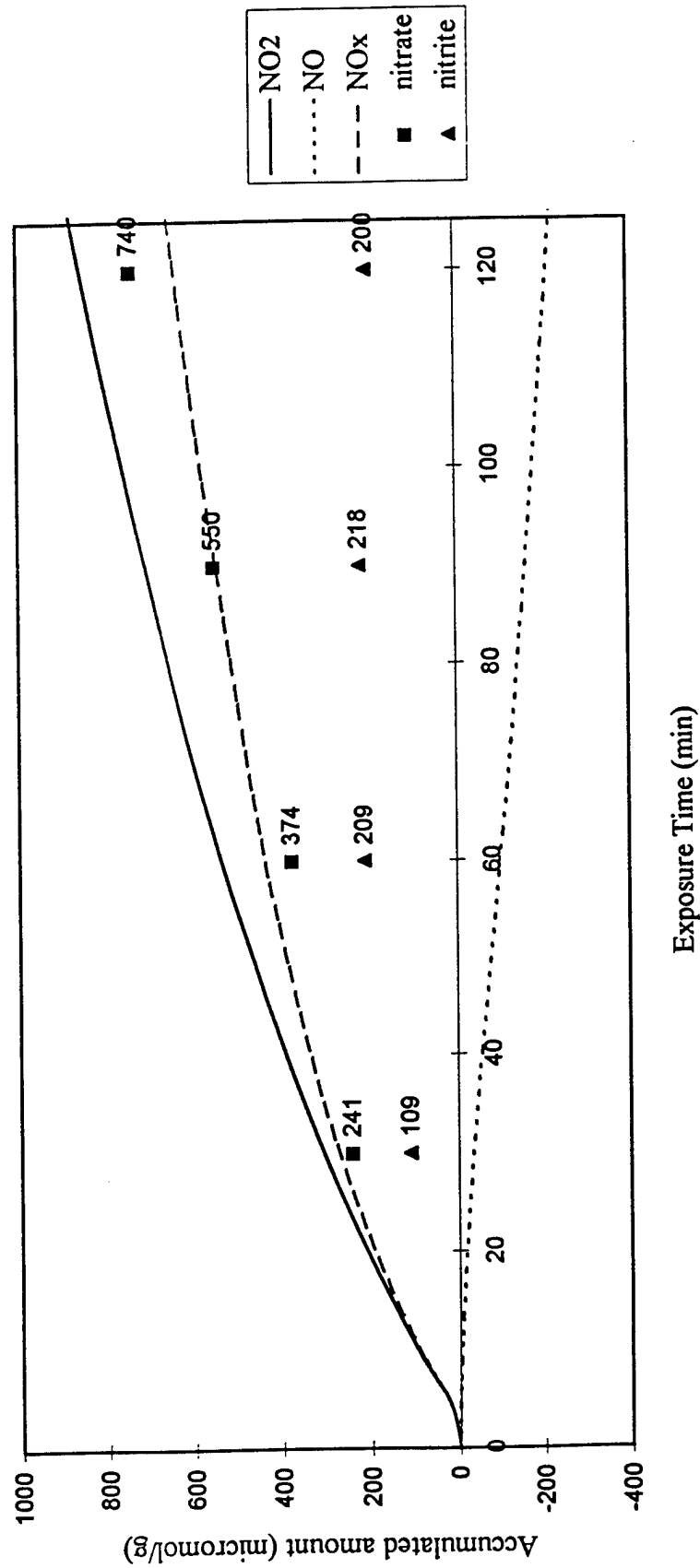
Figure 3-28. Cumulative NO2 and NO Uptake and Nitrate and Nitrite Formation from K2CO3 Longbed, Layer 1, 25C

above in Table 3-6. Though the nitrate and nitrite quantities are overestimated, the trends

in the build up of nitrate and the plateau in nitrite levels are evident.

KOH-treated alumina

The proposed mechanisms for KOH are similar to those for K_2CO_3. Initially:

$$2KOH_{(s)} + 2NO_{2(g)} \rightarrow KNO_{2(s)} + KNO_{3(s)} + H_2O_{(l)} \qquad (3\text{-}11)$$
$$2KOH_{(s)} + NO_{(g)} + NO_{2(g)} \rightarrow 2KNO_{2(s)} + H_2O_{(l)} \qquad (3\text{-}12)$$
$$\text{Overall:} \quad 4KOH_{(s)} + 3NO_{2(g)} + NO_{(g)} \rightarrow KNO_{3(s)} + 3KNO_{2(s)} + 2H_2O_{(l)} \quad (3\text{-}13)$$
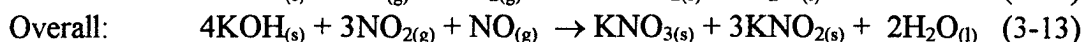
As with K_2CO_3, NO is initially sorbed as all NO_x is taken up. The cumulative NO_x

sorption and formation of nitrate and nitrite are shown in Figure 3-29. Note that the 60

minute run data are questionable, as described earlier. According to reaction (3-13), a 3:1

ratio in moles of nitrite to nitrate should be observed. At an exposure time of 30 minutes,

for the bottom 3 layers of the bed, where the early stages of the mechanism are apparent

this 3:1 ratio is observed. However, the top two layers of the bed at 30 minutes have

already progressed past this initial mechanism as they have been exposed to more NO_x at

30 minutes than the bottom 3 layers. At this point, nitrite reacts with incoming NO_2 to

form nitrate and NO. KOH may still sorb NO_2:

$$2KOH_{(s)} + 2NO_{2(g)} \rightarrow KNO_{2(s)} + KNO_{3(s)} + H_2O_{(l)} \qquad (3\text{-}11)$$
$$KNO_{2(s)} + NO_{2(g)} \rightarrow KNO_{3(s)} + NO_{(g)} \qquad (3\text{-}14)$$
$$\text{Overall:} \quad 2KOH_{(s)} + 3NO_{2(g)} \rightarrow 2KNO_{3(s)} + NO_{(g)} + H_2O_{(l)} \qquad (3\text{-}15)$$
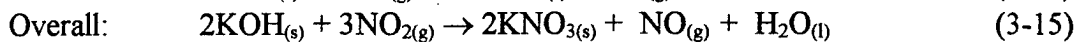
As for the case with K_2CO_3, potassium nitrite which is formed is more stable and less

reactive with incoming NO_2 than aluminum nitrite on untreated alumina. This delays NO

production until sufficient NO_x has penetrated the bed to cause a shift from the initial
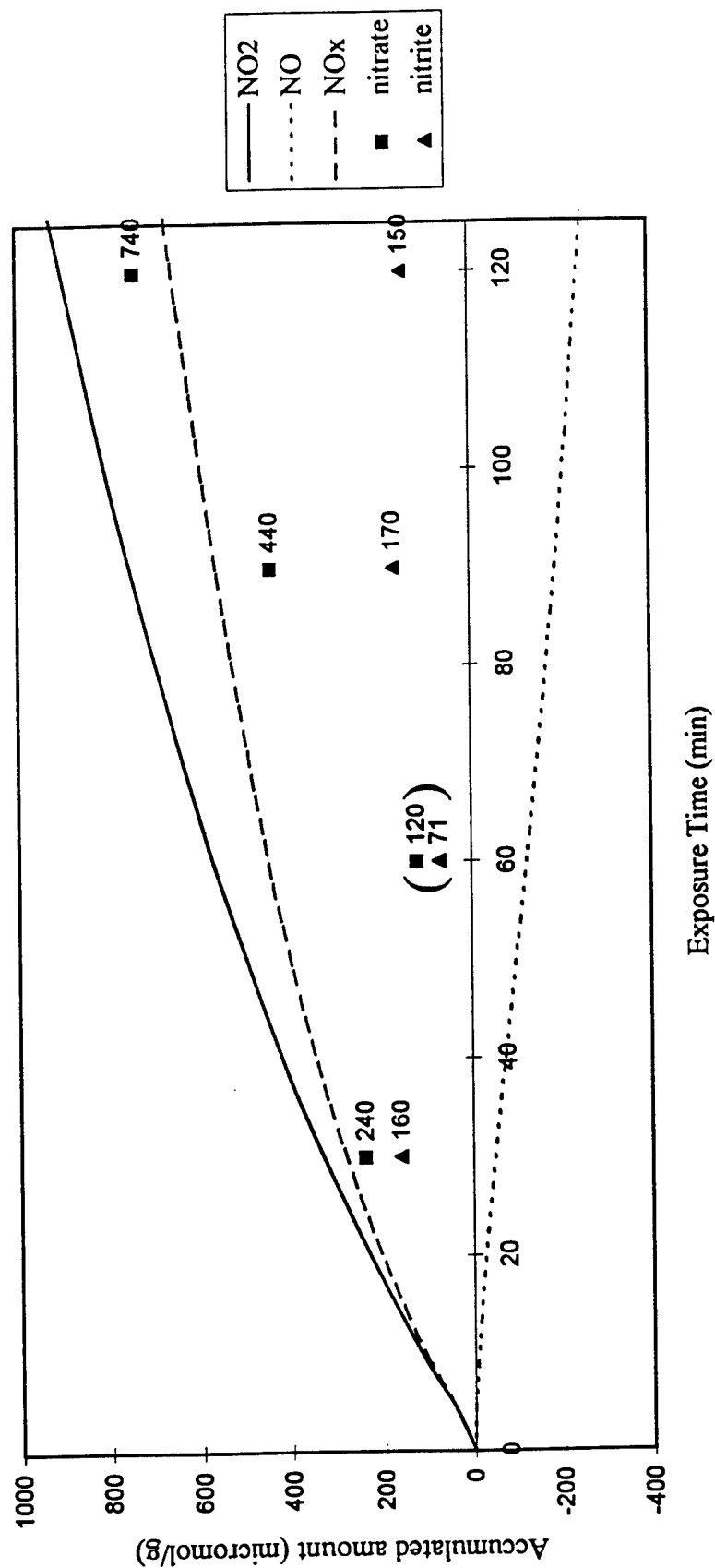
Figure 3-29. Cumulative NO2 and NO Uptake and Nitrate and Nitrite Formation from KOH Longbed, Layer 1, 25C

mechanism to the latter. In Figure 3-29, the build up of nitrate and the corresponding

leveling off of nitrite is evident.

Confirmation of Sorption Mechanisms

In order to obtain better percent recoveries (NO_x^- formed / NO_x sorbed), several

alumina samples were tested for nitrate and nitrite immediately after exposure to NO_x.

These samples displayed percent recoveries better than those of the longbed series and are

included here to provide further evidence in support of the sorption mechanisms proposed

in the previous section of this thesis.

Short-term and long-term exposures

As the proposed mechanisms for the treated aluminas indicate a change in sorptive

activity as exposure to NO_x increases, samples were tested for nitrate and nitrite for both

short and long term exposures. The samples which were exposed to NO_x for a short time

period are shown in Figure 3-30. These samples (Figure 3-30) were all exposed to an

airstream containing mostly NO_2 (1950 ppm) with a trace of NO (<10 ppm,) at 25°C,

which was the same airstream and temperature used for the longbed series. These samples

consisted of three grams of alumina and were exposed to NO_x for less than 20 minutes.

The percent recoveries for these samples were 102%, 116%, and 101% for the untreated,

K_2CO_3-treated, and the KOH-treated samples, respectively. In Figure 3-30 for the

untreated sample, the proposed ratios of 3 moles of NO_2 sorbed to 1 mole of NO

produced and of 3 moles of NO_2 sorbed to 2 moles of nitrate formed in the overall

mechanism (3-5) are confirmed by the experimental results. For the treated aluminas, the
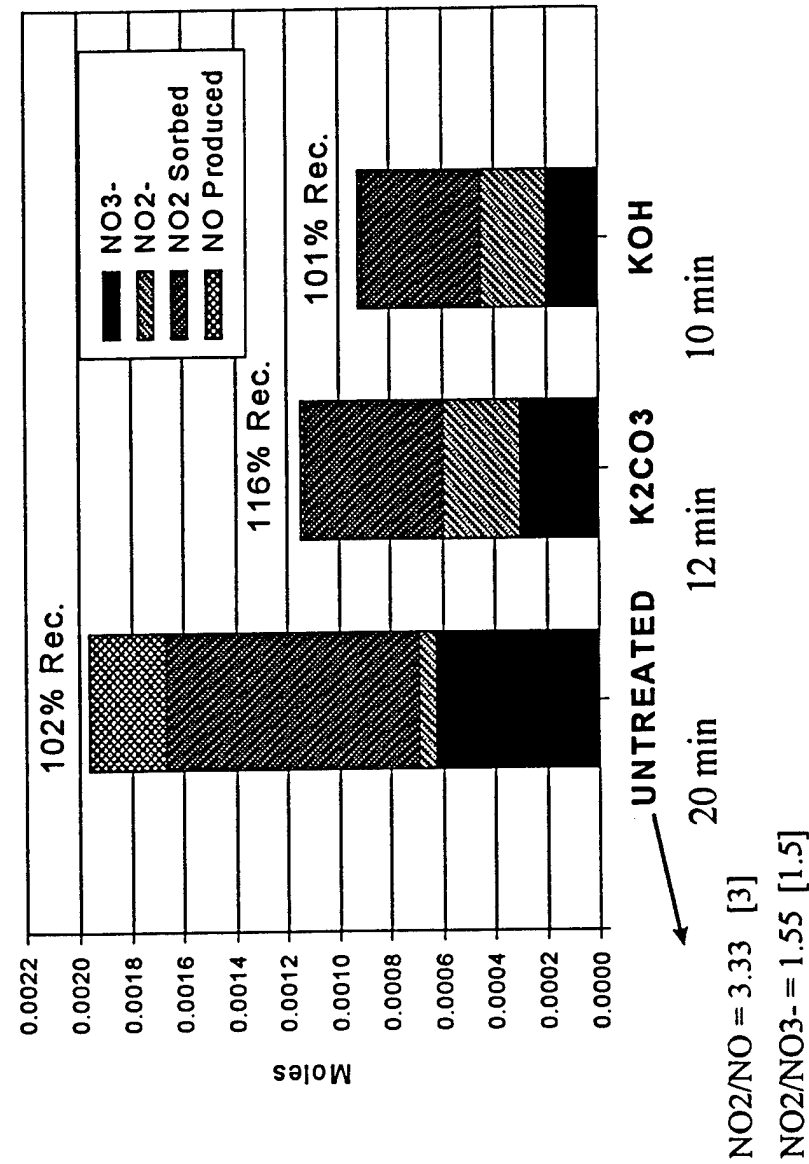
Figure 3-30. Moles of NOx Sorbed and NOx- Formed During Short-Term Exposures to Identical NOx Airstreams

ratio of 2 moles of NO_2 sorbed to 1 mole of nitrite or nitrate formed, which is proposed in the initial mechanisms (3-6 and 3-11), is confirmed. Note that since NO is present only in trace quantities, only the sorption of NO_2 is evident and therefore the second and overall reactions in the initial mechanisms proposed for the treated aluminas are not applicable to this situation.

In Figure 3-31 are shown the corresponding results for a KOH-treated sample tested for nitrate and nitrite for both short-term (14 minutes) and long-term (800 minutes) exposures to NO_x with an airstream consisting of 500 ppm of both NO_2 and NO. Only the KOH-treated sample is included here as the mechanisms for KOH-treated and K_2CO_3-treated alumina are essentially the same. There is no time dependence associated with the untreated alumina mechanism. In Figure 3-31, NO is initially sorbed for the 14 minute exposure whereas NO is produced over the 800 minute exposure. The second equation of the initial mechanism (3-12) is confirmed for the short-term exposure in Figure 3-31 as the molar ratios of the observed species are in good agreement with those proposed in (3-12). It appears that for this situation, where NO and NO_2 are of similar concentrations, reaction (3-12) dominates and the formation of nitrite is heavily favored over that of nitrate. For the long-term exposure, the reaction in (3-15) for the overall mechanism at longer exposures is confirmed through the agreement of the observed and proposed molar ratios of the active species. In Figure 3-31, as exposure to NO_x increases for the treated aluminas, nitrate formation is favored as the nitrite which was formed earlier can react with incoming NO_2 to form nitrate and produce NO.

500:500 ppm (NO2:NO), 25C

800 min, 3g

94% Rec.

Legend: NO3-, NO2-, NO2 Sorbed, NO Sorbed

Moles (0.010, 0.009, 0.008, 0.007, 0.006, 0.005, 0.004, 0.003, 0.002, 0.001, 0.000, -0.001, -0.002)

KOH

$2KOH_{(s)} + 3NO_{2(g)} \longrightarrow 2KNO_{3(s)} + NO_{(g)} + H_2O_{(l)}$

NO2-/NO3- = .32 [→0]   NO2/NO = -3.96 [-3]

NO2/NO3- = 1.87 [1.5]

14 min, 3g

101% Rec.

Legend: NO3-, NO2-, NO2 Sorbed, NO Sorbed

Moles (0.0008, 0.0007, 0.0006, 0.0005, 0.0004, 0.0003, 0.0002, 0.0001, 0.0000)

KOH

$2KOH_{(s)} + 2NO_{2(g)} \longrightarrow KNO_{2(s)} + KNO_{3(s)} + H_2O_{(l)}$

(NO2)/NO2- = 0.604 [2]   NO2-/NO3- = 9.18 [1]

(NO2)/NO3- = 5.5404 [2]

$2KOH_{(s)} + NO_{(g)} + NO_{2(g)} \longrightarrow 2KNO_{2(s)} + H_2O_{(l)}$

(NO2+NO)/NO2- = 1.09 [1]   NO2-/NO = 2.04 [2]

Figure 3-31. Moles of NOx Sorbed and NOx- Formed During Short-Term and Long-Term Exposures to Identical NOx Airstreams for KOH-Treated Alumina

Temperature

Effects of bed temperature were also explored for samples which were tested for nitrate and nitrite immediately after exposure to NO_x and which displayed percent recoveries close to 100%. The ratio of nitrite to nitrate formed on each of the three sample types which were exposed to NO_x under identical conditions are shown in Figure 3-32. The samples were exposed for 120 minutes to an airstream of 500 ppm of both NO_2 and NO at temperatures of 25°C and 250°C. Figure 3-32 illustrates that the formation of nitrite is favored at the higher temperature for all three sorbents. However, this nitrite formation is much more significant for the treated aluminas whereas for untreated alumina the amount of nitrite formed is still minimal when compared to that of nitrate (note the scales of the charts in Figure 3-32). This situation indicates that the second reaction (sorption of NO and NO_2) in the initial mechanism proposed for the treated aluminas is favored under these conditions.
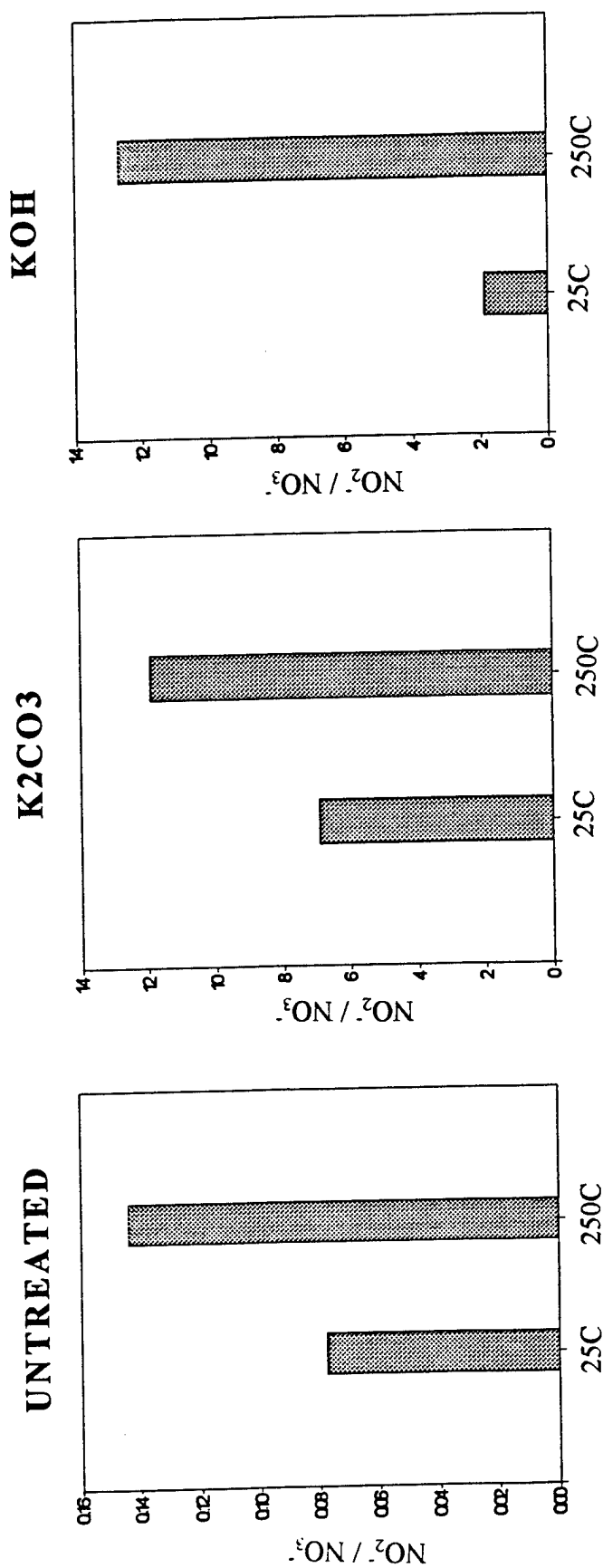
Figure 3-32. Ratios of Nitrite to Nitrate Formed for 120 Minute Exposures to Identical NOx Airstreams at Temperatures of 25C and 250C

CHAPTER 4
CONCLUSIONS AND RECOMMENDATIONS

The goals of the research described here were to develop a method for

quantification of nitrate and nitrite on NO_x-exposed alumina, and with this knowledge,

gain understanding into the nature of the NO_x-alumina interactions in the adsorption

process. The following results were obtained from this study:

- An electrochemical analytical method using Ion-Specific Electrodes (ISEs) was

  shown to be reasonably reliable in the quantification of nitrate and nitrite formed

  on alumina surfaces exposed to NO_x gas. Though the systematic error varied

  from -20 to +20%, the method allowed for the use of correction factors. The

  errors observed were probably due in part to the varying ionic strengths between

  standards and samples, particularly for the K_2CO_3-treated samples.

- The pH of the alumina material was primarily dependent upon the treatment

  (coating) used. Nitrate concentration affected pH on a smaller scale. No

  effect on pH from nitrite was observed with exposed alumina samples, though

  this may have been due to the fact that for the samples tested, nitrate was most

  often present in greater concentrations than nitrite. The pH of K_2CO_3-treated

  alumina samples was typically 10 to 11. For KOH-treated alumina, typical pH

  values ranged from 11 to 12. The pH of untreated alumina samples varied from

4 to 6. In samples containing higher levels of nitrate (> .001M), the pH tended to be towards the lower end of these ranges.

- K_2CO_3-treated alumina was the most effective sorbent for NO_x as more moles of nitrate and nitrite were found on this material than on the others for identical exposures to NO_x. KOH-treated alumina was also effective as a NO_x adsorbent. These findings are consistent with those of Lee (1998) and Lee et al. (1998a and 1998b).

- Untreated alumina, while being an improvement over other materials tested for NO_x adsorbency in recent history such as MgO/v, does not have the adsorbent capacity for NO_x displayed by the alkaline-treated aluminas. In this way, alumina is more valuable in NO_x adsorption as a support material for other compounds. Though alumina itself is a fairly effective adsorbent material, the enhanced NO_x sorption by the coated alumina occurs at the NO_x-alkaline compound interface.

- While the alkaline-treated aluminas are effective adsorbers of NO_2 gas, NO gas is produced in this process. This NO production was delayed most for K_2CO_3-treated alumina, and also to a lesser degree for KOH-treated alumina. This action may be attributable to the stability of the potassium nitrite which is formed in the alkaline environment. The pH of the K_2CO_3-treated alumina used in this study corresponds to the pH range of optimal nitrite recovery observed by other researchers (Choi and Fung, 1980). Initially, NO was sorbed by the treated materials, particularly for K_2CO_3-treated alumina, but as exposure time to NO_2

gas increased, NO was inevitably produced.

- The observation that NO is sorbed by the treated materials only when NO_2 is also present in an airstream indicates that a simultaneous reaction occurs at the surface of the sorbent which involves these two species and the treatment compound. Untreated alumina does not appear to significantly sorb NO. The treated aluminas displayed the capacity to effectively sorb both NO and NO_2. Sorption of NO by the treated aluminas was most pronounced when the concentration of NO in the airstream was similar to that of NO_2 and bed temperature was increased (> 200°C).

- The 3:1 molar ratio of NO_2 sorbed to NO produced which has been observed by previous researchers was verified in this study for untreated alumina and was indicated for the alkaline materials tested.

- The stability of the potassium nitrite formed on the treated materials during NO_x sorption delayed formation of NO gas as the reactions in (3-9) and (3-14) were initially impeded. As exposure time to NO_x increased, the reactions in (3-9) and (3-14) became more important and NO production was enhanced.

- The mechanisms proposed for the adsorption processes are simplified models that describe possible reactions occurring at the NO_x-sorbent interface. Though some of the expected relationships proposed in the mechanisms were observed, it was impossible to verify all of these relationships in this study. It is possible that the reaction of NO, NO_2, and the treatment compound forms a N_xO_y compound, such as N_2O_3, which may be an important regulator in the adsorption of NO_x by

the alkaline sorbents. Detection, identification, and quantification of these compounds, if in fact they are present, would pose a considerable challenge.

- The effects of temperature on nitrate and nitrite quantities on alumina sorbents were briefly explored in this study. For the treated aluminas, sorption of NO and the associated formation of nitrite is favored as temperature is increased.

In future studies involving electrochemical analytical methods for nitrate and nitrite quantification of alumina-NO_x interactions the following points should be addressed:

- Attempts at improving the overall accuracy of the ISE testing method should be made. Investigations into the addition of buffers and/or ionic strength adjustors to standards and samples consistent with those used by Milham et al. (1970), Morie et al. (1972), or Choi and Fung (1980), may be worthwhile, particularly for K_2CO_3-treated alumina samples.

- For long-term, high volume studies, the ISE method is not recommended as it is fairly tedious and time consuming. Though instrumental response is fast for ISEs, preparation of standards and samples to ensure reliable results is rather laborious as fresh standards need to be made each testing day. Automated methods such as Ion Chromatography (IC) would be more efficient for long-term projects, though a reliable filtration system would be needed to prevent fine alumina particles in the sample solutions from fouling the column. The ISE method is well-suited for intermediate and/or short-term testing.

APPENDIX A

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF
pH, [NO3-], and [NO2-] OF NOx-EXPOSED ALUMINA ADSORBENTS
IN AQUEOUS SOLUTIONS

SECTION 1

SCOPE AND APPLICATION

1.1   This method is applicable to the determination of hydrogen, nitrate, and nitrite ion activity present on NOx-exposed alumina. The alumina is put into solution to allow for electrochemical characterizations. A pH electrode is used to determine solution pH. Separate analyses are undertaken to quantify nitrate and nitrite levels by using ion-specific electrodes (ISE's). A Markson Model 4603 Solution Analyzer and Corning Model 245 pH Meters were used for pH and NOx-ion analyses, respectively.

1.2   Alumina is in the pellet form. Sample type is classified by the coating (treatment) which has been impregnated or precipitated on the alumina before exposure to NOx. The following methods describe procedures for the characterization of untreated, potassium carbonate-treated, and potassium hydroxide-treated aluminas.

SECTION 2

SUMMARY OF METHOD

2.1   The degree of acidity in a sample is most typically quantified through pH measurement. The definition of pH is:

$$pH = -\log [H_3O^+]$$

where the concentration is in moles per liter. The lower the pH of a sample, the greater the acidity of that sample.

The system used for pH measurement was a Corning (model 476086) combination electrode with a Markson (model 4603) Solution Analyzer.

2.2   The measured potential corresponding to the level of specific ion in solution is described by the Nernst equation:

$$E = E_0 + S \log(A)$$

            where:

E = measured electrode potential, mV

E_0 = reference potential (constant), mV

A = ion level in solution (activity)

and   S = electrode slope (about -53 to -60 mV per decade increase)

The level of specific ion, A, is the activity or 'effective concentration' of that specific ion in solution. The total concentration of the specific ion in solution includes both bound or complexed ions as well as free (unattached) ions:

$$C_F = C_T - C_B$$

where:

C_F = concentration of free ions

C_T = total ion concentration

and C_B = concentration of ions in bound or complexed forms

The ion activity is related to the free ion concentration by the activity coefficient (γ):

$$A = \gamma\, C_F$$

Ionic activity coefficients are variable and largely depend on total ionic strength. Ionic strength is defined as:

$$IS = \tfrac{1}{2}\, \Sigma C_1 Z_1^2 + C_2 Z_2^2 \, ... C_i Z_i^2$$

where:

IS = ionic strength

C_i = concentration of ion i

and Z_i = charge of ion i

If the background ionic strength is high and constant relative to the sensed ion concentration, the activity coefficient is constant and the activity is directly proportional to concentration (Orion Research Inc., 1991). In order to equalize the ionic strength between the sample and the standard solutions, the latter were designed to simulate the composition of the sample solution.

The methods for nitrate and nitrite quantification are briefly summarized:

1)   Nitrate concentration is determined by taking the nitrite out of the sample through the addition of sulfamic acid and measurement of solution

potential in a half-cell with an Orion Nitrate Ion-Specific Electrode (model 93-07).

2)   Nitrite concentration is also determined electrochemically in a half-cell system. The presence of nitrate causes an interference with the measurement of nitrite. No dependable way of removing this interference was found so the nitrite standards are 'contaminated' with nitrate so as to give them the same nitrate concentration as determined in the sample. The sample is then directly measured with an Orion Nitrite Ion-Specific Electrode (model 93-46) and the nitrite concentration determined from calibration. In this way the nitrate interference is ignored as it is present at equal levels between the sample and standards.

The addition of acidic and basic compounds to the samples and standards for nitrate and nitrite measurements is necessary to equalize the pH of the sample with that of the standards (equalizing pH helps keep ionic strength constant). Also the ISE's have specific pH operating ranges which, if not complied with, will yield unsatisfactory results.

SECTION 3

CALIBRATION AND ANALYSIS WITH MARKSON MODEL 4603 SOLUTION ANALYZER AND ORION MODEL 245 pH METER

3.1   The equipment and reagents needed for these determinations include:

1) a Markson Model 4603 Solution Analyzer,

2) a Corning Model 476086 pH electrode,

3) an Orion Nitrate Ion Specific Electrode, model 93-07,

4) an Orion Nitrite Ion Specific Electrode, model 93-46,

5) a Corning Single Junction Electrode, model 90-01,

6) a Corning Model 245 pH meter,

7) a Fisher Scientific Stirring Hot Plate,

8) 50 and 150 mL beakers,

9) Specific volume pipettes and flasks,

10) 1M K_2CO_3 solution,

11) 1M KOH solution,

12) 1M sulfamic acid solution,

13) 10% sulfuric acid solution,

14) Orion Nitrate Ionic Strength Adjustor 930711,

15) Orion Double Junction Reference Filling Solution 900002,

16) Orion Optimum Results F Filling Solution 900046,

17) 3 M KCl solution,

18) pH buffer solutions of pH 3, 7, and 10,

19) 25, 50, and 200 mL graduated cylinders.

3.2   Procedure

1. Prepare electrodes for nitrate analysis. Soak nitrate electrode in de-ionized (DI) water for 15 minutes, then in a 10^{-3} M nitrate solution for an hour. Fill the double-junction reference electrode with fresh solutions (no longer than 3 days old). For the outer chamber solution dilute 2 mL of Nitrate Interference Suppressor Solution to 100 mL with DI water. Disassemble the reference electrode, drain inner solution (a green AgCl solution) and fill with fresh

solution. Reassemble electrode and pipette sufficient outer chamber solution into the outer chamber up to the fill hole. While holding the reference electrode in one hand, press down on the top of the electrode and release quickly to cause a momentary leaking of the fill solution (this ensures that outer chamber solution contacts the electrode membrane).

2. Make 100 mL of 10^{-1}M NO$_3$ standard solution from a compound containing nitrate*. Make serial dilutions of this solution to .05M, .01M, .005 M, .001 M, and .0001M NO$_3$. Be sure to stir the solutions.

3. Make 1M sulfamic acid solution (250 mL if not on hand).

4. Note the volumes of the nitrate standard solutions (70 mL is recommended for the .01, .001, and .0001M solutions; 40 mL is recommended for the .05 and .005M solutions.)

5. Prepare the nitrite electrode and single-junction electrode for analysis. Rinse the nitrite module (the gray sensing tip) with DI water and then place the electrode in nitrite storage solution. This solution is made by adding .1 mL of .1M nitrite solution and 50 mL of Nitrite Interference Suppressor Solution to a 100 mL specific volume flask and filling to volume (100 mL) with DI water. Soak the nitrite electrode in this solution for one to two hours. Fill the single junction reference electrode with Orion Optimum Results F filling solution. Press down on the electrode's cap and release to wet the membrane.

6. Make nitrite standards from a compound containing nitrite. Sodium or potassium nitrite is recommended. Use the same concentrations and volumes as with the nitrate solutions.

7. Obtain a sample of alumina from Max Lee. Record the mass of the amount of alumina in the total (dry) sample and also the mass of alumina to be put in solution (usually 1 gram of the alumina is saved for later decomposition studies). Note: for untreated alumina the pellets must be first powderized and then massed. Place the alumina to be tested into a 150 mL beaker and add 50 mL of de-ionized water. Sonicate the solution for 10 minutes. (Note: data is recorded on pre-made tables titled 'Test Sheet for Alumina Surface Chem').

8. Calibrate the Markson Solution Analyzer for pH. Insert the pH electrode into buffer with pH 7 and adjust the 'standardize pH' knob until the readout displays '7.00'. Rinse electrode with DI water and place in pH 4 buffer. Adjust the slope control on the meter so that '4.00' is displayed. Check the electrode range by rinsing the
electrode and placing it in pH 10 buffer. The value displayed should be close to '10.0'. (The Markson analyzer--Corning electrode system is accurate over a wide range of pH).

9. Insert the pH electrode into the sample solution. Stir solution for 1-2 minutes, stop stirring and allow the solution to sit. The pH reading should stabilize quickly. Record the pH and place electrode back into pH 7 buffer.

10. If the alumina has not been treated (untreated) go to step 11. If the alumina has been treated with K_2CO_3 or KOH go to step 14 (procedure is written for K_2CO_3-treated samples but the treated samples have the same procedure—just substitute KOH for K_2CO_3 if the sample is KOH-treated).

11. Acidify each of the nitrate standards to pH 2.5 by adding sulfamic acid. Calibrate the Corning 245 meter for mV. Set meter to mV mode and insert the double-junction reference electrode and the nitrate electrode into the 10^{-4} M standard. Repeat for the rest of the standards going from low to high nitrate concentrations. Record mV for each standard. Pour about 20 mL of the sample solution into a 25 mL graduated cylinder and record this volume. Transfer this solution to a 50 mL beaker.
Insert the pH electrode into this solution and observe pH. Record the pH on the test sheet. Add sufficient sulfamic acid to the sample to bring the pH of the solution to 2.5. Use the pH electrode to slightly stir the solution when adding the acid. Measure and record mV for the sample solution. Record any changes in sample volume from the addition of the acid. Construct a calibration curve using Microsoft Excel (note: the linear range of the electrode is from .0001M to .05M). Determine nitrate concentration in the sample using the equation from the log regression given by Excel and factoring in any dilution factors. The concentration for the total (original) alumina sample can be found by multiplying the determined concentration by the weight of the alumina in the original sample and dividing by the weight of alumina in the measured sample (note: record all data on the test sheet).

12. Do calculations to determine how much nitrate compound or solution is needed

to contaminate the nitrite standard solutions so as to give them the same nitrate concentration as determined in the sample. Add the specific amount of the nitrate medium to each nitrite standard so that the nitrite standards and sample have equal nitrate concentrations. Calculate and record new standard concentrations if diluted.

13. Calibrate the nitrite electrode with the 'contaminated' standard nitrite solutions. If the pH of the sample solution is between 5 and 7 proceed with mV measurement. If the sample pH is not in this range add dilute sulfuric acid or KOH solution, one drop at a time, until in range. Measure mV for the sample solution. Determine nitrite concentration, see second half of step 11. Go to step 18.

14. Basify standard nitrate solutions to the sample pH by adding K_2CO_3 solution. Acidify the standards to pH 2.5 with sulfamic acid. Calculate and record new

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standard concentrations due to dilution. Take a portion of the sample and add sufficient sulfamic acid so that a reaction (bubbling) is observed. Add extra acid to ensure the reaction is complete (at a pH of around 1.6 all the nitrite should be converted to nitrogen gas). Add K_2CO_3 solution to bring the pH to 2.5.

15. Calibrate mV with these standard nitrate solutions and determine nitrate concentration as in step 11.

16. Perform step 12 with level of nitrate found in step 15.

17. Bacify the 'contaminated' nitrite standards to the sample pH. Acidify original sample and standards to an equal pH between 4 and 8 (working pH range of nitrite ISE) with sulfuric acid. Calibrate mV and determine nitrite concentration in sample as in step 13. Go to step 18.

18. When sample testing has been completed, a system performance test is undertaken. Make an independent sample which contains known levels of nitrate and nitrite and which are close to the levels determined in the sample(s). Make sample pH close to that of the test sample(s) by adding K_2CO_3 or KOH solutions, depending on the type of sample tested (note: disregard if sample was untreated). Depending on the composition of this independent sample, perform the appropriate procedures above to determine nitrate and nitrite levels in the sample. Obtain percent error in the results. Record all data on pre-made tables

titled 'QC TEST SHEET'.

*Use compounds which will not cause interferences with nitrate measurements, see Orion ISE manual for further details. Magnesium, sodium, or potassium nitrates are recommended.

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SECTION 4

QUALITY CONTROL

4.1   At the end of a day's testing, an independent control sample of known concentration is made and analyzed to obtain a measure of the accuracy of the results obtained on that specific day. This independent sample is made to have similar characteristics to the actual samples which were analyzed during the day. The independent 'check' sample should have pH, NOx concentrations, and alumina content similar to those of the tested samples. For independent samples designed to simulate treated samples, the pH of the independent sample is manipulated through the addition of alumina coated with the same treatment material as that for the tested samples. The standard solutions used in the actual sample testing are also used to obtain calibration curves for the check sample. The above procedure(s) are used for NOx^- quantification in the check sample. Percent error in NOx^- concentration is obtained for the check sample from the experimental and actual levels. Data is recorded on sheets labeled 'QC TEST SHEET'. The percent errors for [NO3-] and [NO2-] for the total testing period are presented versus Julian day in system performance charts.

4.2   In the calibration of the Markson pH meter for pH, the pH buffer solutions should

not be used past the expiration date printed on the bottle.

4.3   Fresh standard solutions should be made each day of testing. Levels of the electrode fill solutions should be maintained to a height in the electrode body of at least one inch above the level of the sample being tested to insure adequate flow.

Table A-1. Hourly and daily standard deviations in mV for 5 calibration points for nitrate and nitrite standard solutions

NITRATE

UNTREATED	Hourly Variation						Daily Variation					
Calibration Point	mV	mV	Mv	mV	mV	SD	mV	mV	mV	mV	mV	SD
0.0001	181	184	186	186	186	2.0	169	173	174	172	176	2.3
0.001	125	127	127	126	126	0.7	114	117	121	119	118	2.3
0.005	86	86	87	87	87	0.5	76	82	79	83	81	2.5
0.01	71	71	71	71	71	0.0	63	64	60	64	64	1.5
0.05	39	39	40	40	40	0.5	27	28	28	28	28	0.4

K2CO3	Hourly Variation						Daily Variation					
Calibration Point	mV	mV	mV	mV	mV	SD	mV	mV	mV	mV	mV	SD
0.0001	169	169	169	169	169	0.0	169	173	174	172	176	2.3
0.001	119	119	119	119	119	0.0	114	117	121	119	118	2.3
0.005	81	81	81	81	81	0.0	76	82	79	83	81	2.5
0.01	63	64	64	64	64	0.4	63	64	60	64	64	1.5
0.05	27	28	28	28	28	0.4	27	28	28	28	28	0.4

KOH	Hourly Variation						Daily Variation					
Calibration Point	mV	mV	mV	mV	mV	SD	mV	mV	mV	mV	mV	SD
0.0001	171	171	171	171	171	0.0	171	172	168	170	171	1.4
0.001	119	120	120	120	120	0.4	119	121	122	120	120	1.0
0.005	81	82	82	82	82	0.4	81	80	78	79	82	1.4
0.01	64	64	64	64	64	0.0	59	64	60	62	61	1.7
0.05	28	29	29	28	28	0.5	28	29	29	27	28	0.7

....Table A-1.

NITRITE

UNTREATED

Calibration Point	Hourly Variation						Daily Variation					
	mV	mV	mV	mV	mV	SD	mV	mV	mV	mV	mV	SD
0.0001	113	112	112	110	112	1.0	113	113	111	110	109	1.6
0.001	53	52	52	50	53	1.1	53	51	50	52	51	1.0
0.005	5	6	6	6	5	0.5	5	4	6	2	1	1.9
0.01	-14	-13	-12	-12	-14	0.9	-14	-16	-15	-12	-14	1.3
0.05	-51	-50	-49	-49	-50	0.7	-51	-53	-50	-49	-50	1.4

K2CO3

Calibration Point	Hourly Variation						Daily Variation					
	mV	mV	mV	mV	mV	SD	mV	mV	mV	mV	mV	SD
0.0001	96	94	94	95	93	1.0	96	95	96	92	91	2.1
0.001	39	39	38	38	37	0.7	39	37	38	38	35	1.4
0.005	-2	-4	-4	-4	-5	1.0	81	80	79	78	79	1.0
0.01	-19	-20	-21	-21	-21	0.8	63	62	64	64	63	0.7
0.05	-47	-48	-49	-49	-49	0.8	27	28	28	28	29	0.6

KOH

Calibration Point	Hourly Variation						Daily Variation					
	mV	mV	mV	mV	mV	SD	mV	mV	mV	mV	mV	SD
0.0001	90	86	86	88	90	1.8	90	94	97	92	96	2.6
0.001	33	31	31	32	36	1.9	33	36	44	38	41	3.8
0.005	-2	-4	-4	-1	0	1.6	-2	0	1	-3	0	1.5
0.01	-20	-22	-22	-19	-17	1.9	-20	-18	-16	-20	-17	1.6
0.05	-45	-47	-47	-44	-42	1.9	-48	-51	-49	-49	-48	1.1

APPENDIX B

EXPERIMENTAL DATA TEMPLATES

TEST SHEET FOR ALUMINA SURFACE CHEM

pH =
moles NO3-/g Al2O3 =
moles NO2-/g Al2O3 =

SAMPLE# _____ TOTAL DRY WT. (g) _____

TREATMENT _____ WT. IN SOL'N (g) _____

DATE TESTED _____ VOL. SOL'N (mL) _____

CALIBRATION DATA				CALIBRATION DATA			
[NO3-] (M)	mV			[NO2-] (M)	mV	pH used	[NO3-]
0.0001				0.0001			
0.001		Vo (mL) =		0.001			
0.005		Vf (mL) =		0.005			
0.01				0.01			
0.05				0.05			
SAMPLE			Flue Gas	SAMPLE			
			NOx UP =	Vo (mL) = ____		Vf (mL) = ____	
log reg. eq. _____			temp. =	log reg. eq. _____			
R-squared _____			exp. time (min) =	R-squared _____			
(1) sample [NO3-] _____				sample [NO2-] _____			
(2) adjusted [NO3-]				adjusted [NO2-]			

(2) adjusted [Nox] = (1) x (Vf / Vo)   moles/g Al. = (2) x Vol.Sol'n. / 1000 x mass Al.in sol.

NOTES:

_____

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QC TEST SHEET Date: _____	[NO3] %ERR =
For ___ -Treated Samples	[NO2] %ERR =
Desired pH = _____	

INDEPENDENT SAMPLE	RESULTS FOR INDEPENDENT SAMPLE
[NO3] =	[NO3] =
[NO2] =	[NO2] =
pH =	

LAST CALIBRATION DATA

[NO3-] (M)	mV		[NO2-] (M)	mV	pH used	[NO3-]
0.0001			0.0001			
0.001			0.001			
0.005			0.005			
0.01			0.01			
0.05			0.05			
SAMPLE			SAMPLE			

Vo =   Vf = | Vo =   Vf =

log reg. eq. _____ | log reg. Eq. _____

R-squared _____ | R-squared _____

sample [NO3-] | sample [NO2-]

%ERR = (EXP SAMPLE [NOx] - KNOWN SAMPLE [NOx]) / KNOWN SAMPLE [NOx]

NOTES:

APPENDIX C

QUALITY CONTROL CHARTS
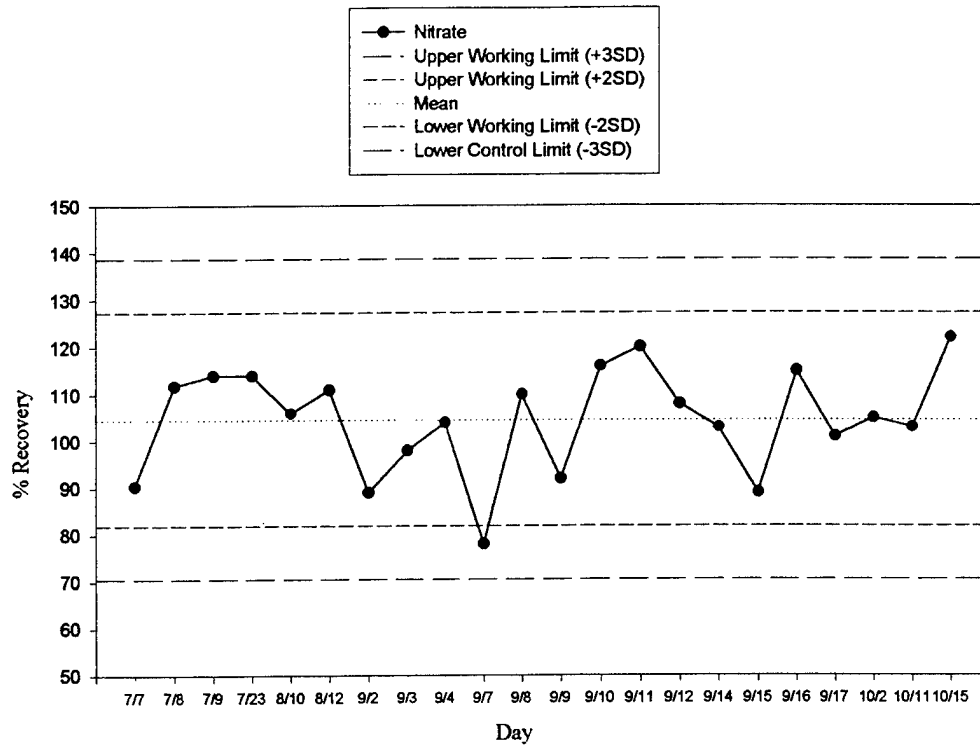
Figure C-1. Quality Control Chart for Nitrate Measurements,
Percent Recovery in Assayed Samples of Known Concentrations
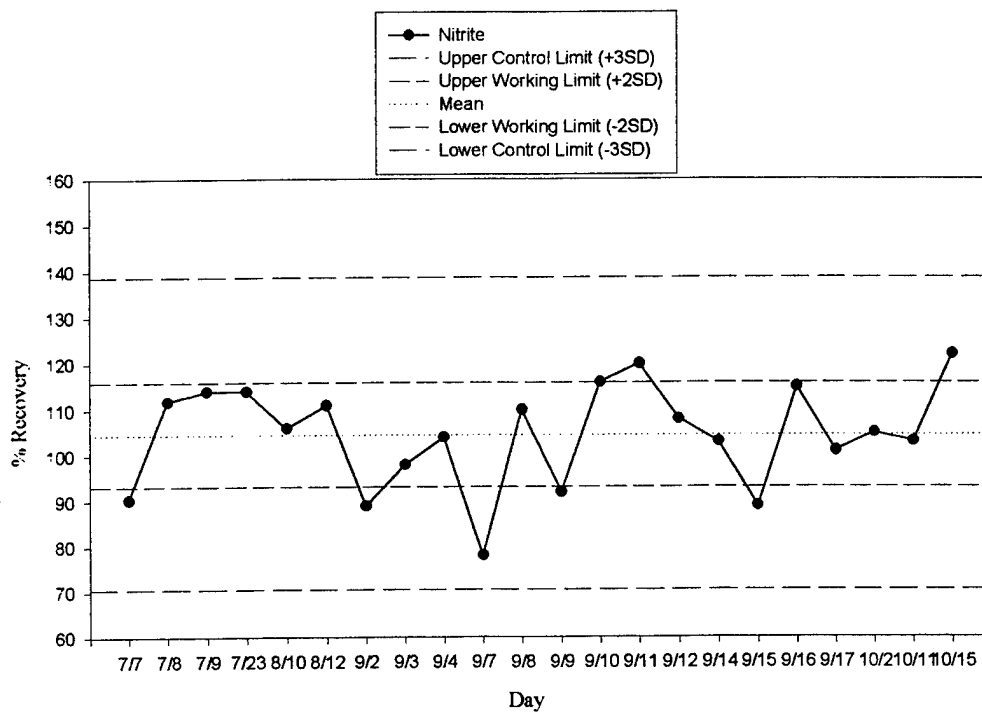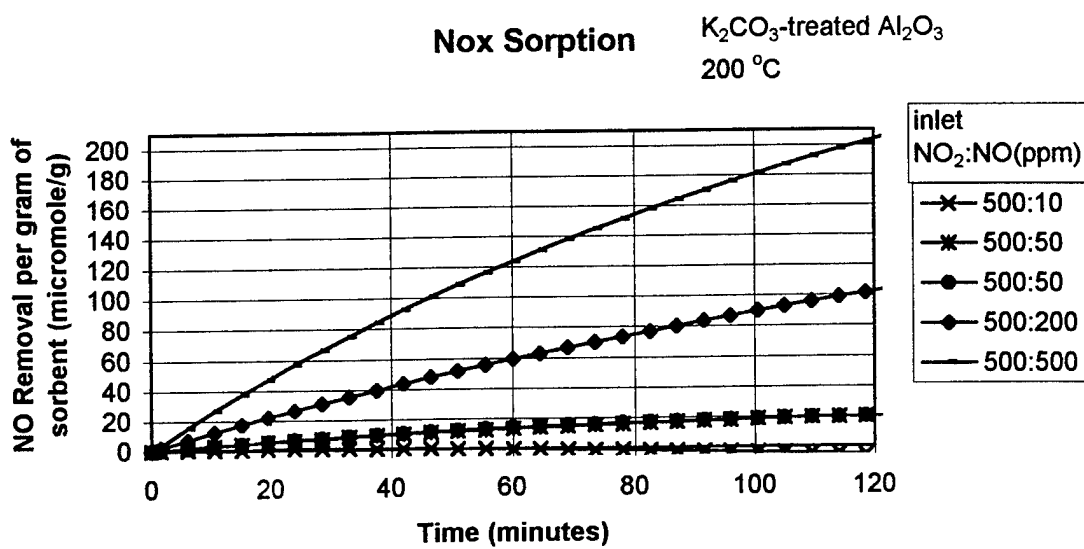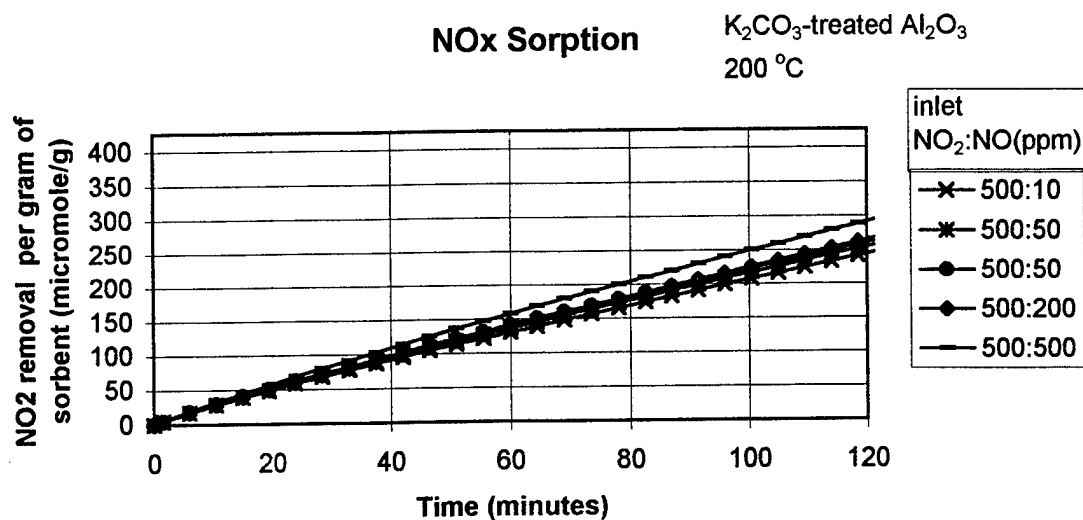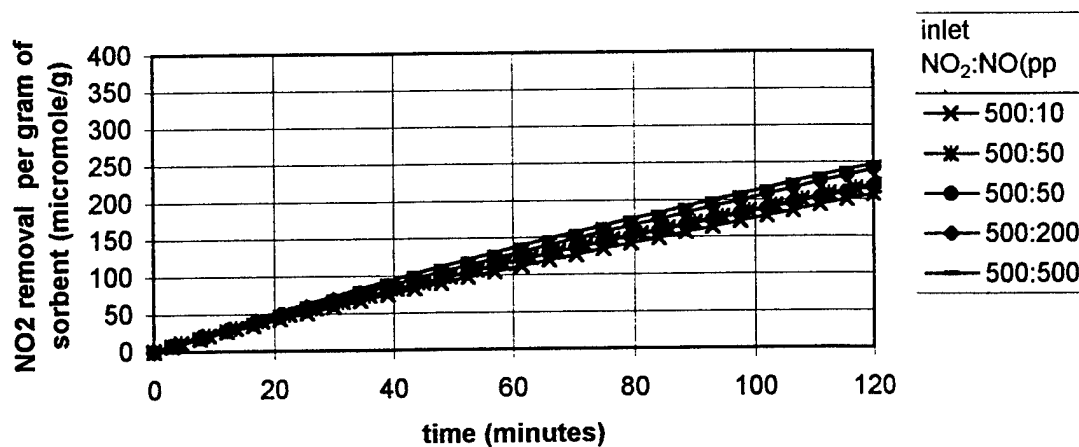for the Main Testing Period

Figure C-2. Quality Control Chart for Nitrite Measurements,
Percent Recovery in Assayed Samples of Known Concentrations
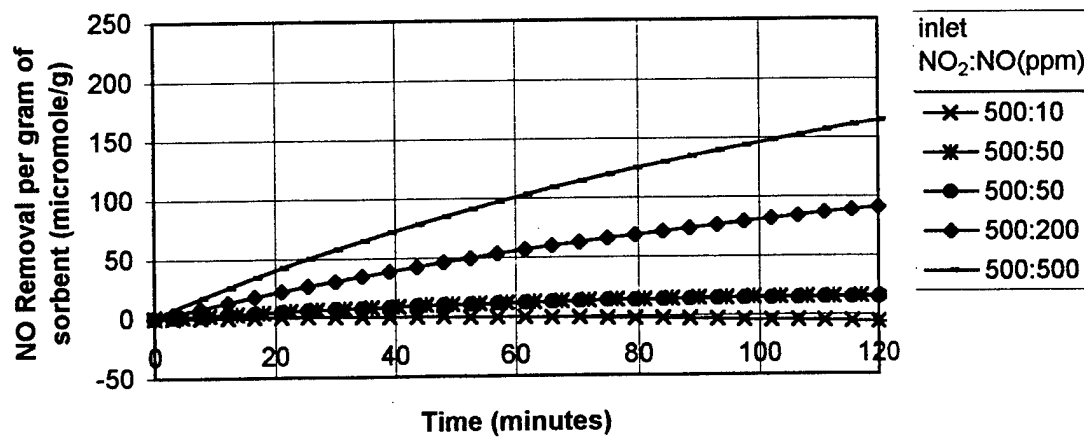for the Main Testing Period

APPENDIX D

SURFACE NITRATE AND NITRITE AND GASEOUS UPTAKE DATA

NOx Sorption from Varied NO Series

NOx Sorption K_2CO_3-treated Al_2O_3 200 °C

inlet NO_2:NO(ppm)

—✕— 500:10
—✶— 500:50
—●— 500:50
—◆— 500:200
——— 500:500

Nox Sorption K_2CO_3-treated Al_2O_3 200 °C

inlet NO_2:NO(ppm)

—✕— 500:10
—✶— 500:50
—●— 500:50
—◆— 500:200
——— 500:500

NOx Sorption KOH-treated Al_2O_3
200 °C

Nox Sorption KOH-treated Al_2O_3
200 °C

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Table 3-5. NOx Sorbed and Nitrate and Nitrite Formed from the K2CO3-Treated Longbed

3g

Exp. Time	K2CO3 NO umol/g	NO2 umol/g	NO2/NO	total umole NO	NO2	NO+NO2	total umole NO3-	NO2-	ratio total NOx-/total NOx
30	-38	318	-8.4	-114	954	840	870	360	1.250
60	-107	554	-5.2	-321	1662	1341	1350	690	1.304
90	-170	730	-4.3	-510	2190	1680	1830	720	1.371
120	-218	861	-3.9	-654	2583	1929	2250	660	1.462

6g

Exp. Time	K2CO3 NO umol/g	NO2 umol/g	NO2/NO	total umole NO	NO2	NO+NO2	total umole NO3-	NO2-	ratio total NOx-/total NOx
30	-15	260	-17.3	-90	1560	1470	1059	750	1.231
60	-68	487	-7.2	-408	2922	2514	1980	1290	1.301
90	-131	670	-5.1	-786	4020	3234	2700	1350	1.252
120	-187	820	-4.4	-1122	4920	3798	4020	1410	1.430

9g

Exp. Time	K2CO3 NO umol/g	NO2 umol/g	NO2/NO	total umole NO	NO2	NO+NO2	total umole NO3-	NO2-	ratio total NOx-/total NOx
30	-2.8	210	-75.0	-25.2	1890	1864.8	1158	1017	1.166
60	-31	419	-13.5	-279	3771	3492	2172	1800	1.137
90	-84	601	-7.2	-756	5409	4653	3180	2070	1.128
120	-137	760	-5.5	-1233	6840	5607	4770	2280	1.257

12g

Exp. Time	K2CO3 NO umol/g	NO2 umol/g	NO2/NO	total umole NO	NO2	NO+NO2	total umole NO3-	NO2-	ratio total NOx-/total NOx
30	0.07	164	2343	0.84	1968	1968.84	1185.3	1128	1.175
60	-11	339	-30.8	-132	4068	3936	2220	2076	1.091
90	-44	504	-11.5	-528	6048	5520	3360	2730	1.103
120	-86	650	-7.6	-1032	7800	6768	5070	2970	1.188

15g

Exp. Time	K2CO3 NO umol/g	NO2 umol/g	NO2/NO	total umole NO	NO2	NO+NO2	total umole NO3-	NO2-	ratio total NOx-/total NOx
30	0.3	134	446.7	4.5	2010	2014.5	1201.5	1164	1.174
60	-5.5	277	-50.4	-82.5	4155	4072.5	2243.4	2343	1.126
90	-26	414	-15.9	-390	6210	5820	3441	3180	1.138
120	-55	540	-9.8	-825	8100	7275	5169	3450	1.185

AVG 1.22
SD 0.11

Table 3-5. NOx Sorbed and Nitrate and Nitrite Formed from the KOH-Treated Longbed

3g KOH

Exp. Time	NO umol/g	NO2 umol/g	NO2/NO	total umole NO	total umole NO2	NO+NO2	total umole NO3-	total umole NO2-	ratio total NOx-/total NOx
30	-53	344	-6.5	-159	1032	873	720	480	1.375
60	-130	590	-4.5	-390	1770	1380	360	213	0.415
90	-191	755	-4.0	-573	2265	1692	1320	510	1.082
120	-246	907	-3.7	-738	2721	1983	2220	450	1.346

6g KOH

Exp. Time	NO umol/g	NO2 umol/g	NO2/NO	total umole NO	total umole NO2	NO+NO2	total umole NO3-	total umole NO2-	ratio total NOx-/total NOx
30	-25	278	-11.1	-150	1668	1518	1050	900	1.285
60	-94	512	-5.4	-564	3072	2508	606	510	0.445
90	-161	695	-4.3	-966	4170	3204	2430	1080	1.096
120	-222	854	-3.8	-1332	5124	3792	3600	900	1.187

9g KOH

Exp. Time	NO umol/g	NO2 umol/g	NO2/NO	total umole NO	total umole NO2	NO+NO2	total umole NO3-	total umole NO2-	ratio total NOx-/total NOx
30	-8.4	216	-25.7	-75.6	1944	1868.4	1140	1170	1.236
60	-51	419	-8.2	-459	3771	3312	813	930	0.526
90	-105	585	-5.6	-945	5265	4320	2694	1650	1.006
120	-161	745	-4.6	-1449	6705	5256	4440	1590	1.147

12g KOH

Exp. Time	NO umol/g	NO2 umol/g	NO2/NO	total umole NO	total umole NO2	NO+NO2	total umole NO3-	total umole NO2-	ratio total NOx-/total NOx
30	-0.67	172	-256.7	-8.04	2064	2055.96	1188	1338	1.229
60	-21	345	-16.4	-252	4140	3888	939	1470	0.620
90	-59	500	-8.5	-708	6000	5292	2817	2130	0.935
120	-107	657	-6.1	-1284	7884	6600	4665	2160	1.034

15g KOH

Exp. Time	NO umol/g	NO2 umol/g	NO2/NO	total umole NO	total umole NO2	NO+NO2	total umole NO3-	total umole NO2-	ratio total NOx-/total NOx
30	-0.4	140	-350.0	-6	2100	2094	1212.9	1419	1.257
60	-15	280	-18.7	-225	4200	3975	1011	1800	0.707
90	-40	412	-10.3	-600	6180	5580	2880	2550	0.973
120	-74	547	-7.4	-1110	8205	7095	4740	2640	1.040

AVG	1.00
SD	3.60

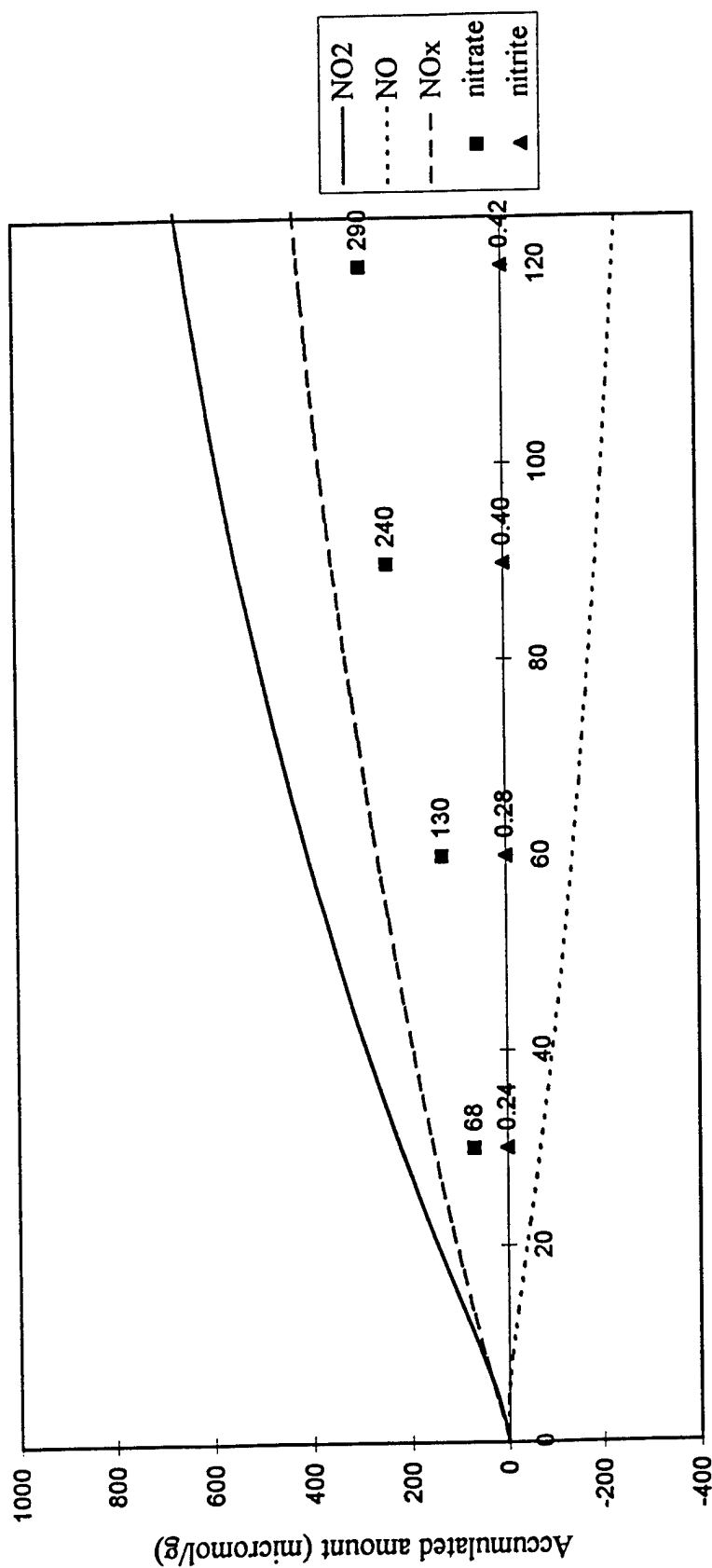*Note: 60 minute data is invalid and is not used in quantitative analyses

Figure D-27(2). Cumulative NO2 and NO uptake and Nitrate and Nitrite
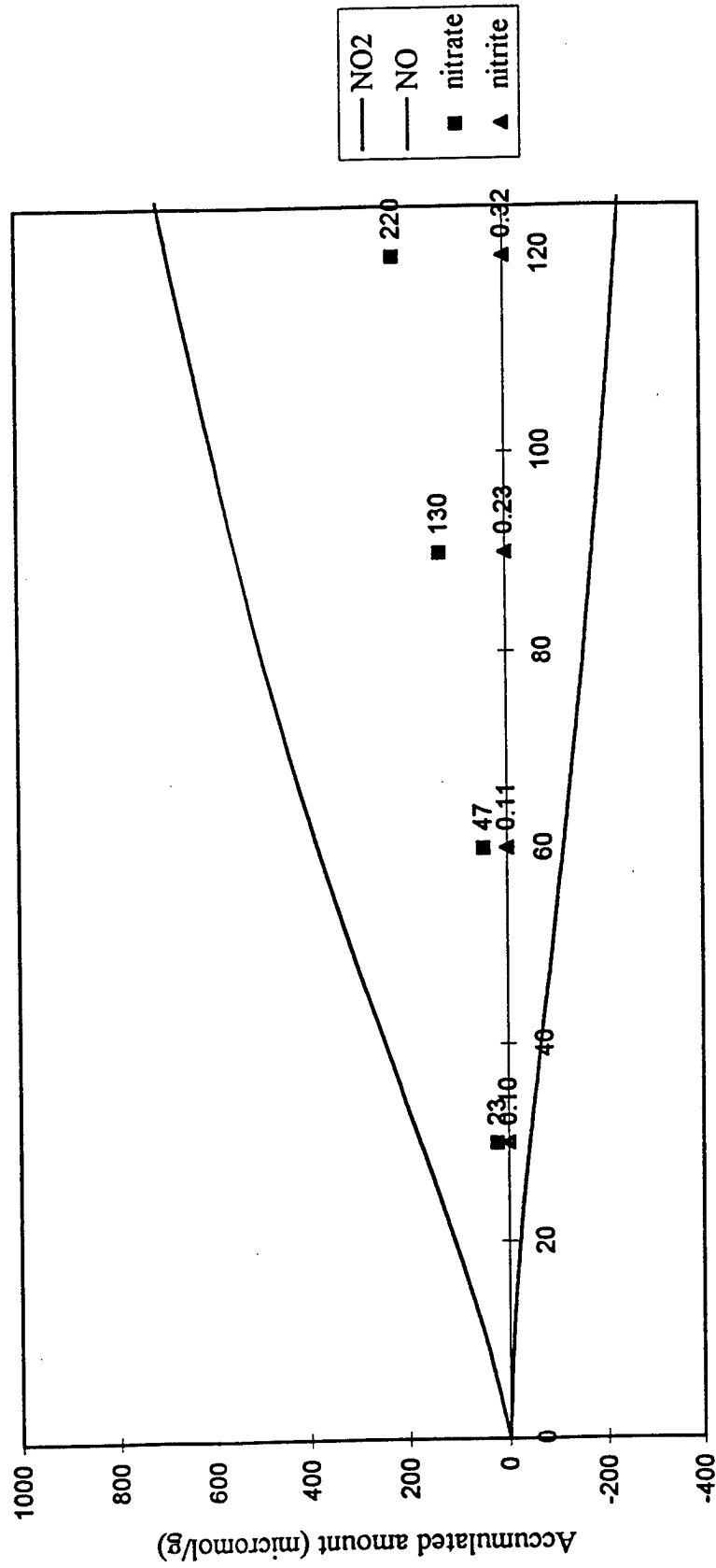Formation from Untreated Longbed, Layer 2, 25C

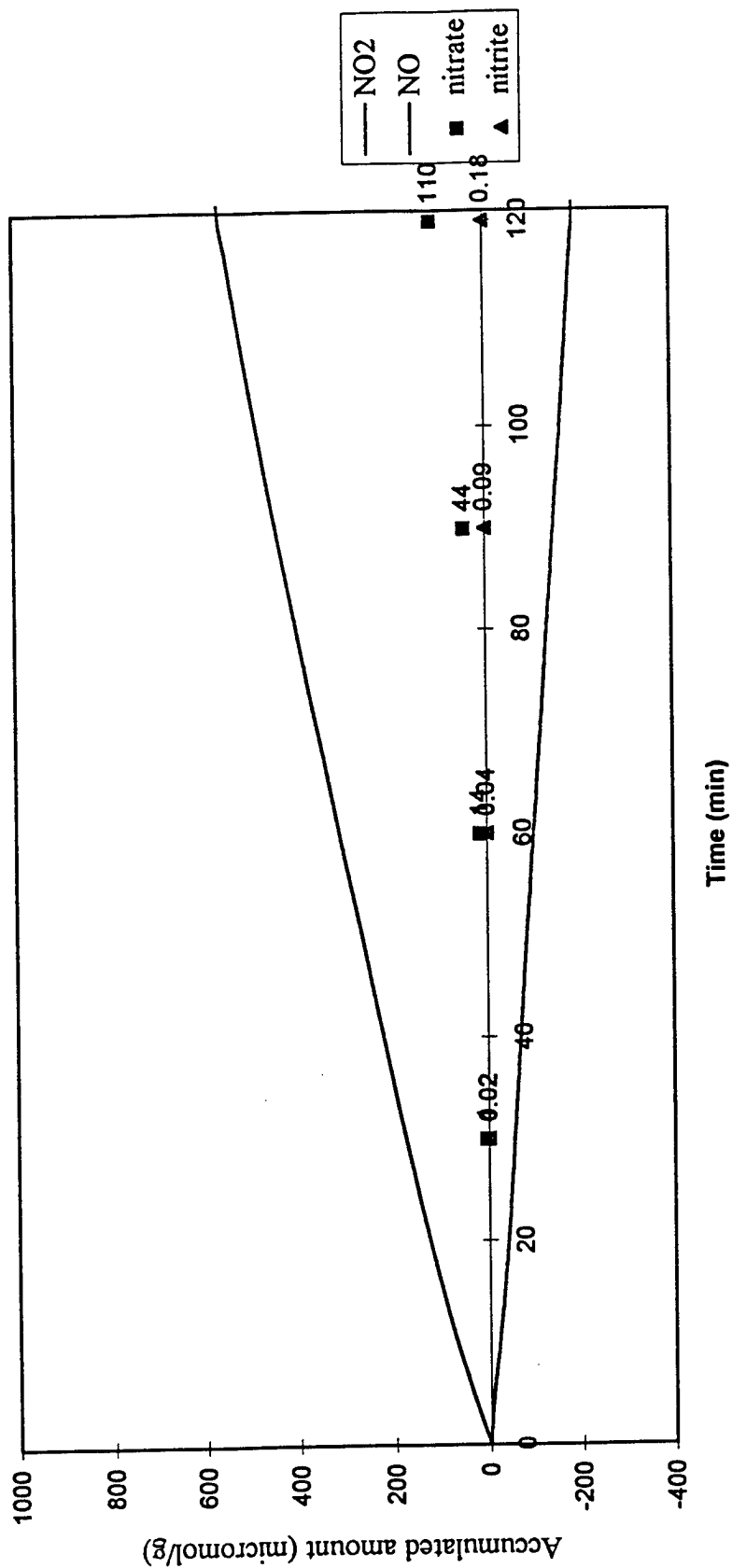Figure D-27(3). Cumulative NO2 and NO uptake and Nitrate and Nitrite Formation from Untreated Longbed, Layer 3, 25C

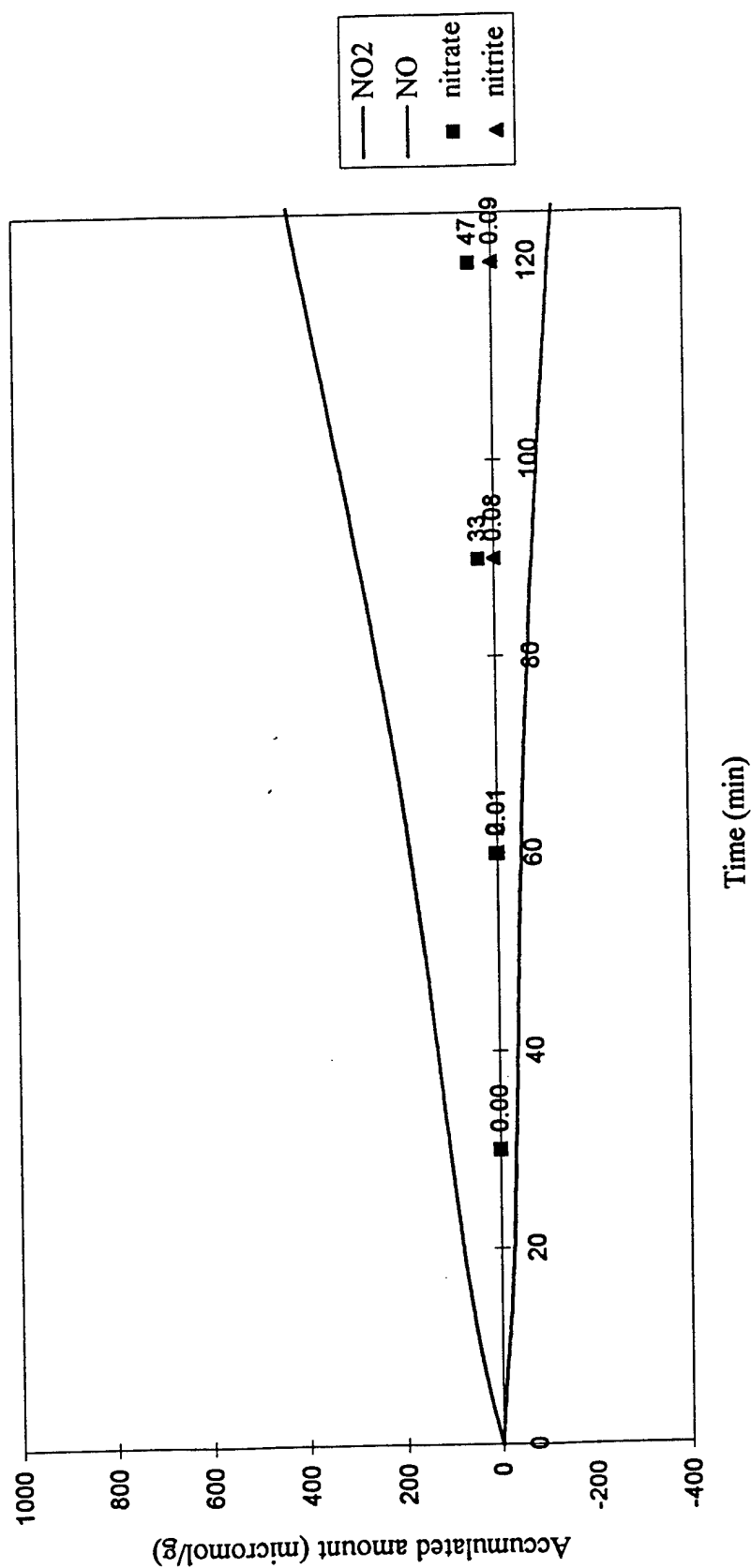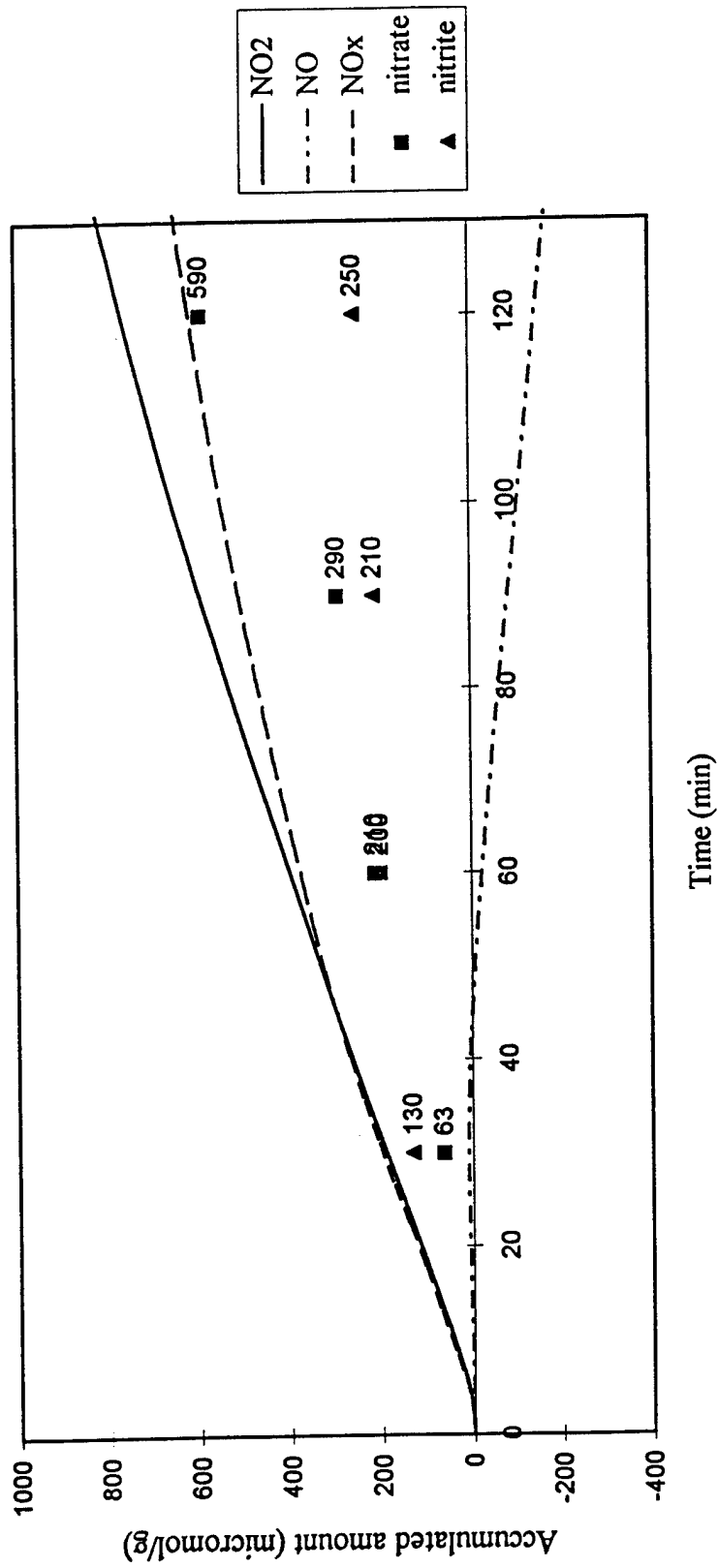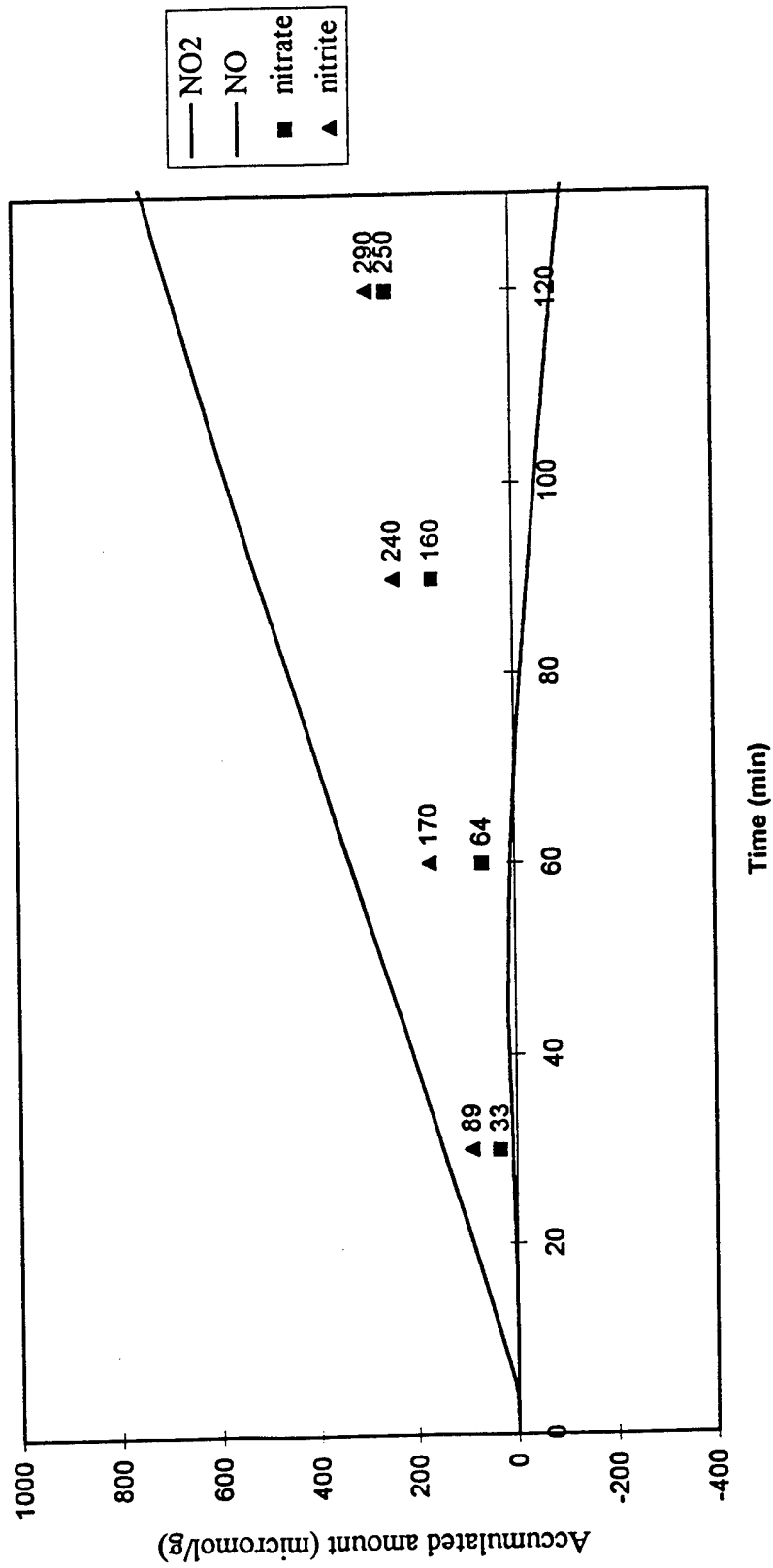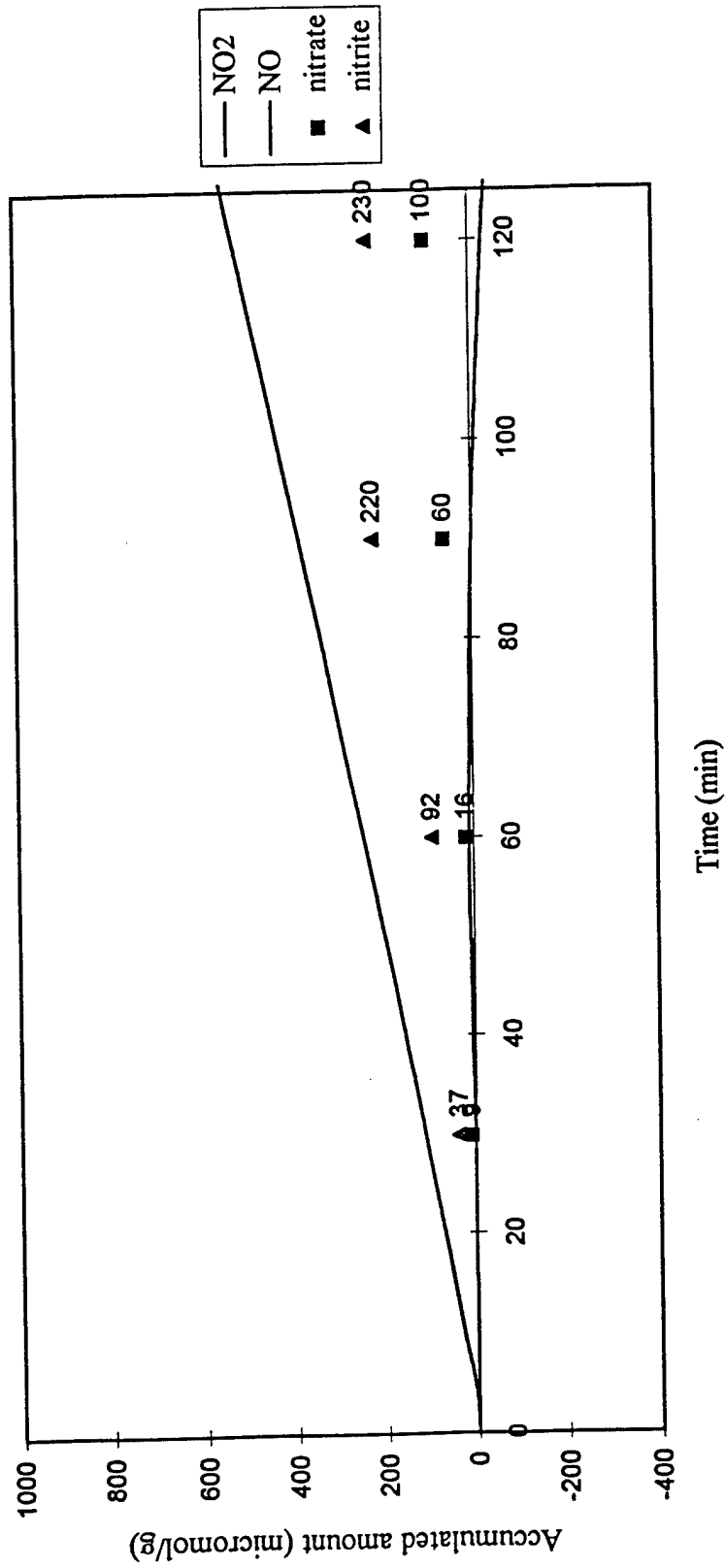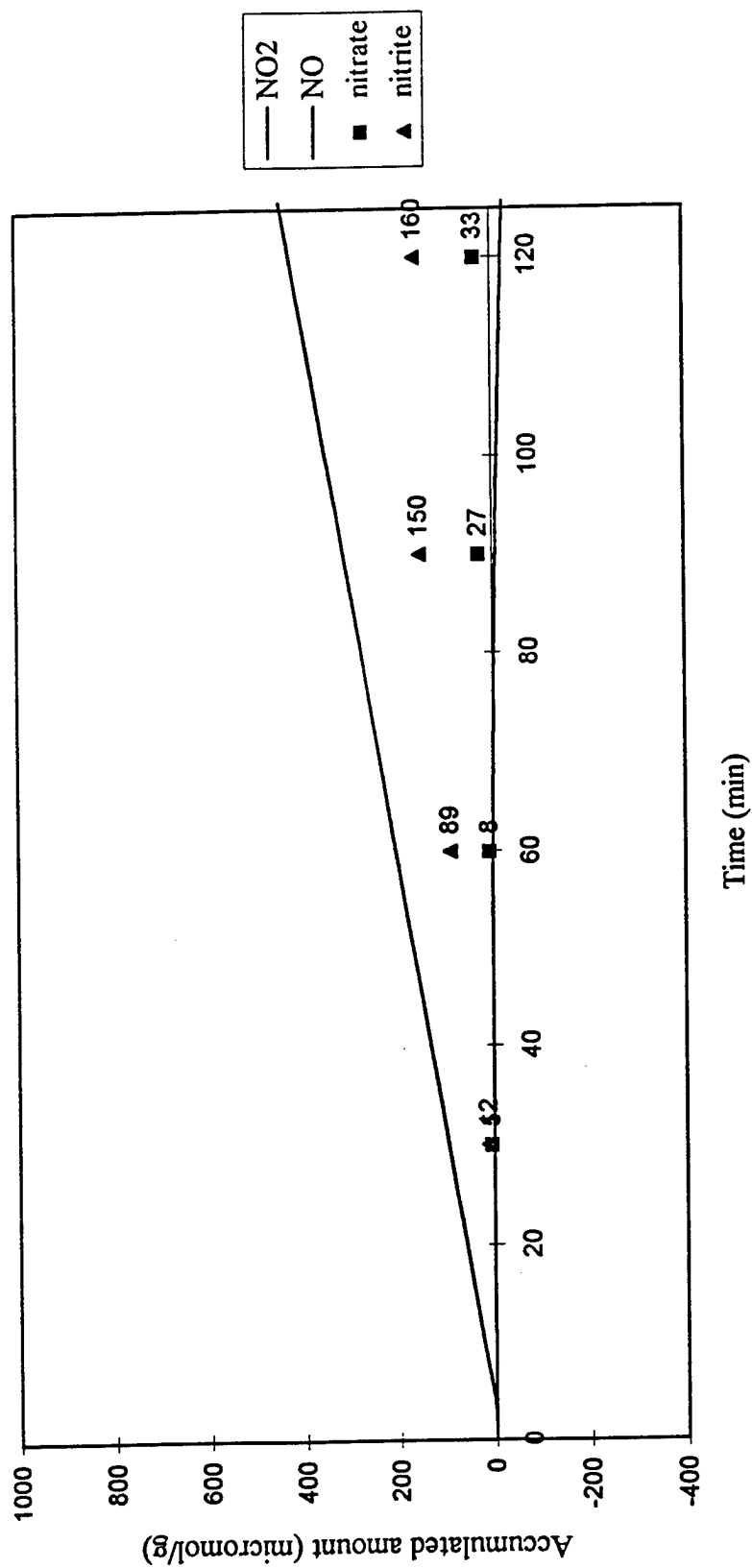Figure D-27(4). Cumulative NO2 and NO uptake and Nitrate and Nitrite Formation from Untreated Longbed, Layer 4, 25C

Time (min)

Figure D-27(5). Cumulative NO2 and NO uptake and Nitrate and Nitrite Formation from Untreated Longbed, Layer 5, 25C
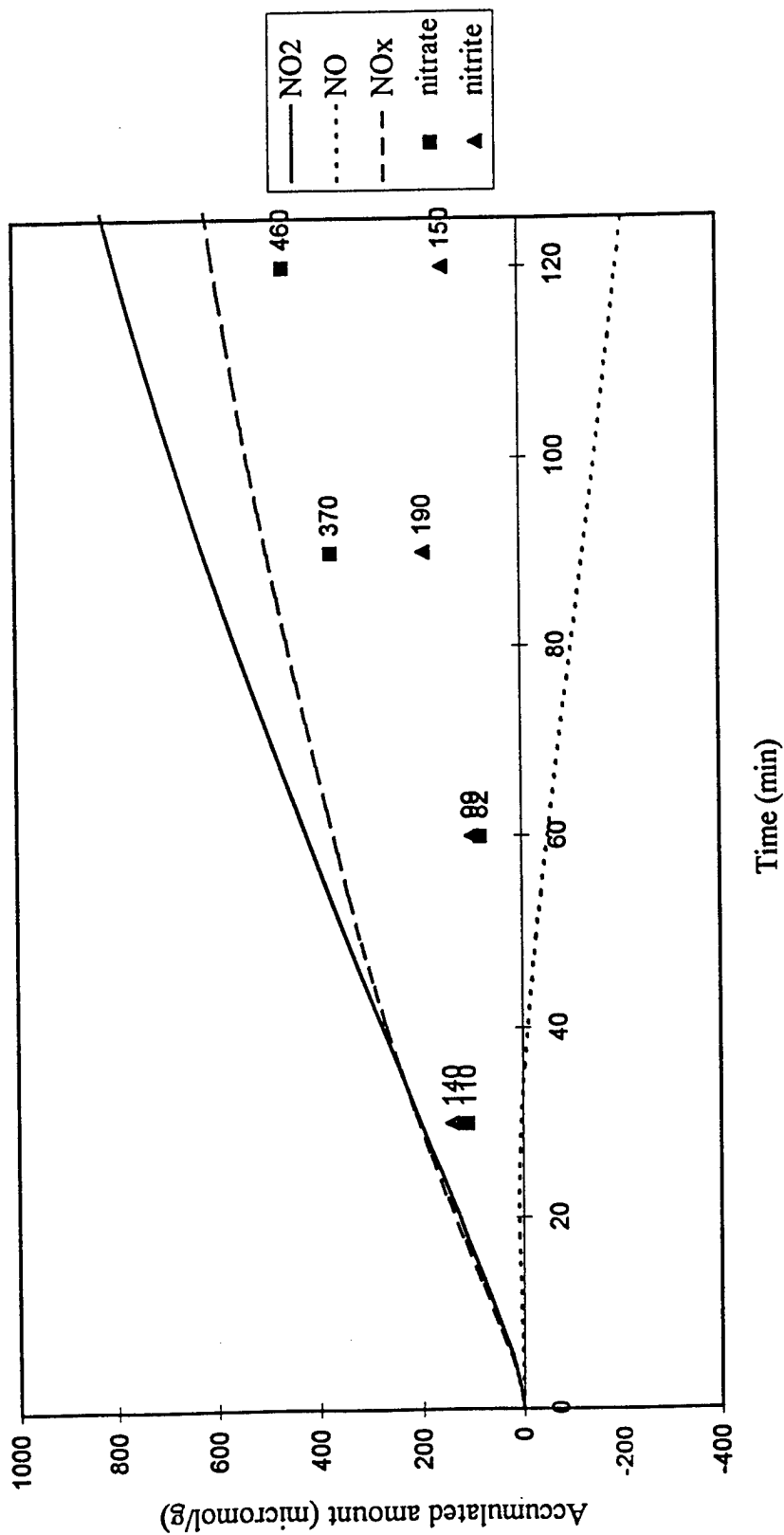
Figure D-28(2). Cumulative NO2 and NO uptake and Nitrate and Nitrite Formation from K2CO3-Treated Longbed, Layer 2, 25C

Figure D-28(3). Cumulative NO2 and NO uptake and Nitrate and Nitrite Formation from K2CO3-Treated Longbed, Layer 3, 25C

Figure D-28(4). Cumulative NO2 and NO uptake and Nitrate and Nitrite Formation from K2CO3-Treated Longbed, Layer 4, 25C

Figure D-28(5). Cumulative NO2 and NO uptake and Nitrate and Nitrite Formation from K2CO3-Treated Longbed, Layer 5, 25C

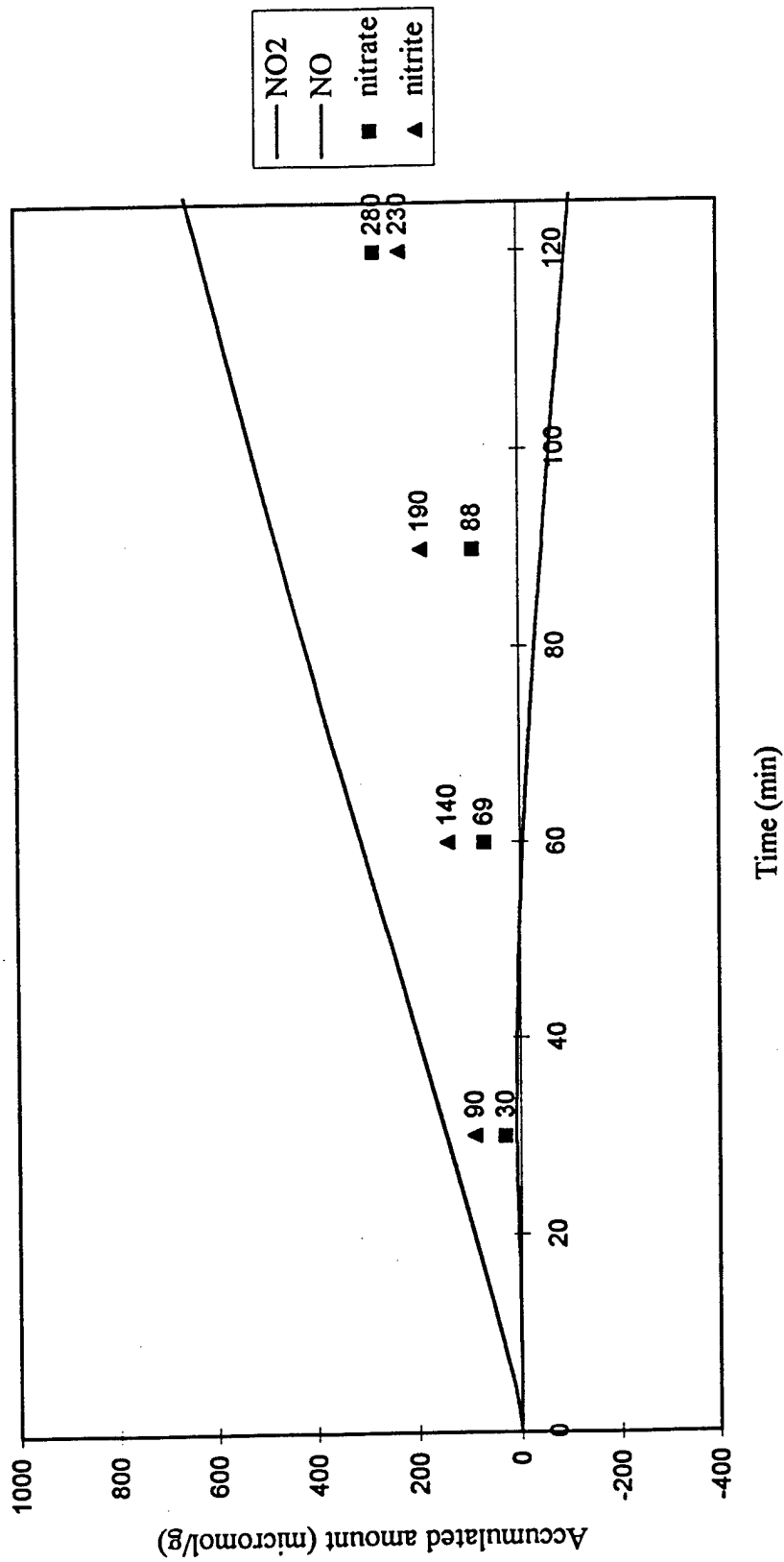Figure D-29(2). Cumulative NO2 and NO uptake and Nitrate and Nitrite Formation from KOH-Treated Longbed, Layer 2, 25C

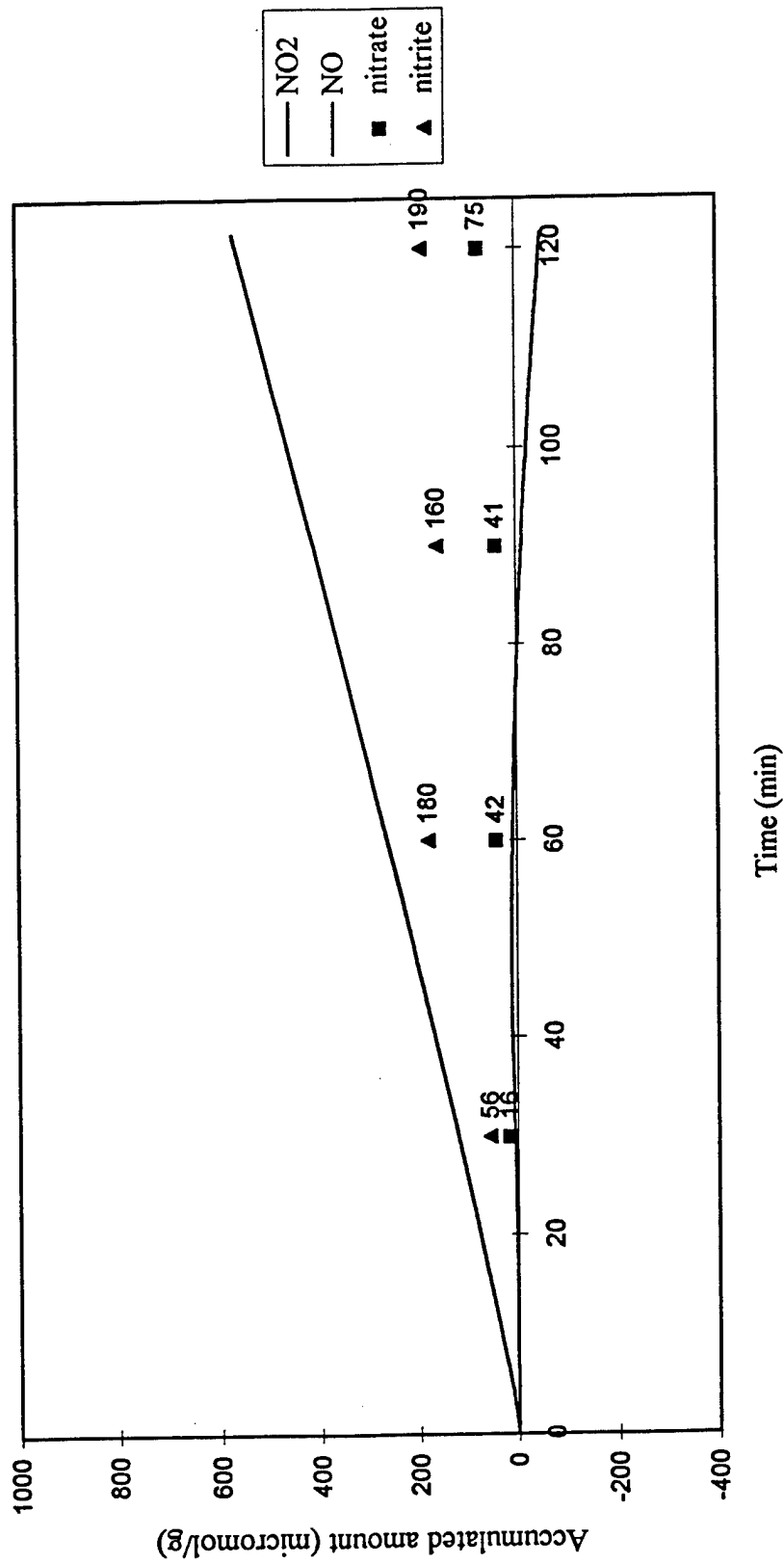Figure D-29(3). Cumulative NO2 and NO uptake and Nitrate and Nitrite Formation from KOH-Treated Longbed, Layer 3, 25C

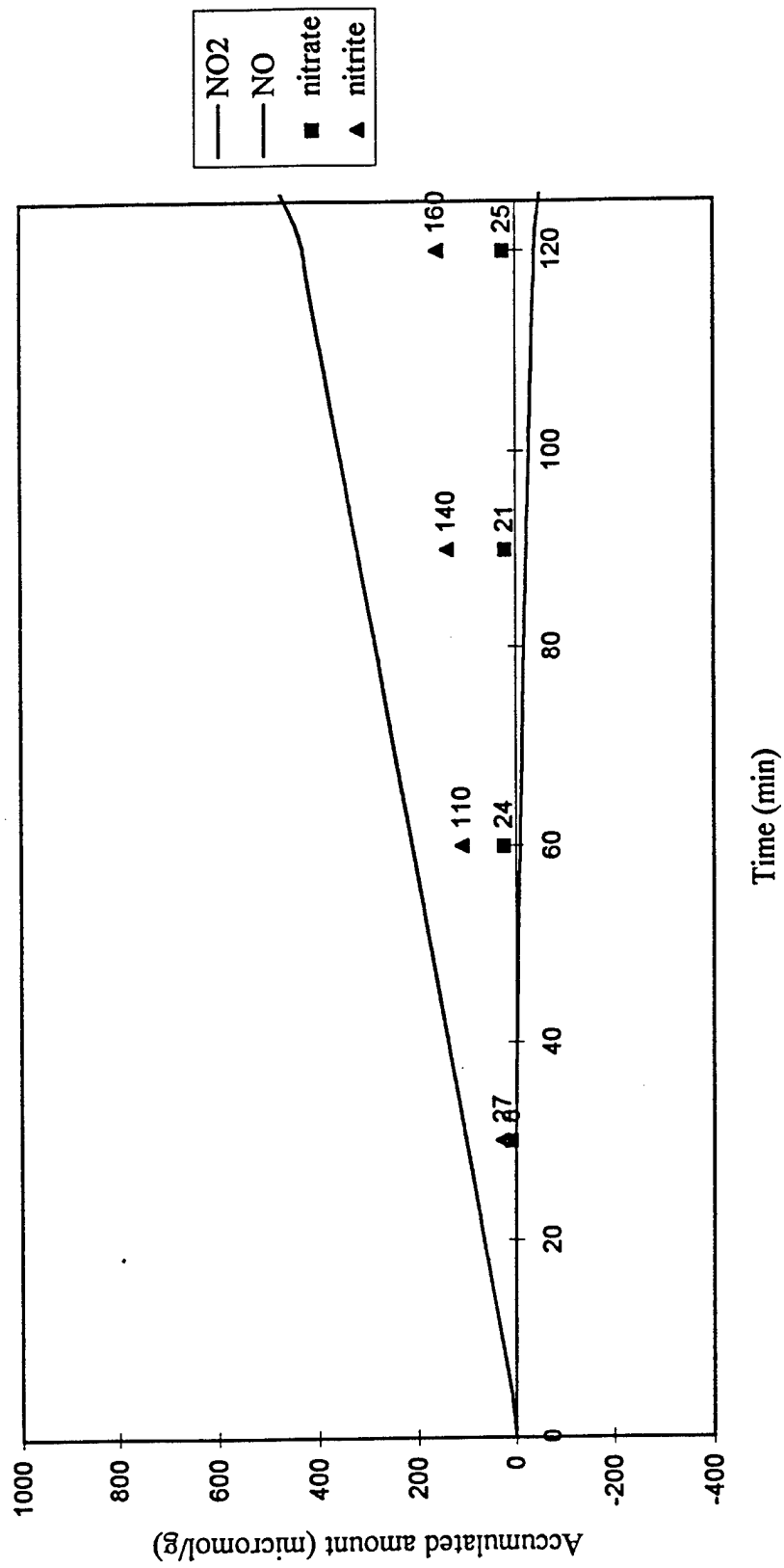Figure D-29(4). Cumulative NO2 and NO uptake and Nitrate and Nitrite Formation from KOH-Treated Longbed, Layer 4, 25C

Figure D-29(5). Cumulative NO2 and NO uptake and Nitrate and Nitrite Formation from KOH-Treated Longbed, Layer 5, 25C

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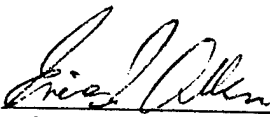
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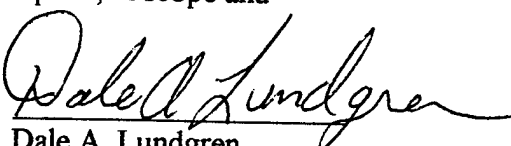Wark, K. and Warner, C.F. *Air Pollution, Its Origin and Control*. Harper and Row, New York, 1994.

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David A. Pocengal was born November 26, 1974, in Johnson City, NY. He received his Bachelor of Arts degree in physics from Ithaca College in Ithaca, NY, in 1996. He was accepted into the Department of Environmental Engineering Sciences at the University of Florida in Gainesville in 1997 to pursue a Master of Science degree with a concentration in air pollution.
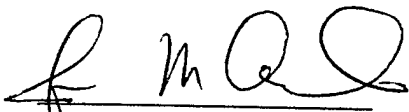
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Eric R. Allen, Chair
Professor of
Environmental
Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Dale A. Lundgren
Professor of
Environmental
Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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This thesis was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Master of Science.

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